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(54) Title: OLEFIN POLYMERIZATION PROCESS

(57) Abstract

Disclosed herein is a process for the polymerization of ethylene, norbornenes and styrenes, by contacting in solution a selected nickel compound and a selected compound which is or can be coordinated to the nickel with the olefin(s). The polymers produced are useful for films and molding resins.

TITLE

OLEFIN POLYMERIZATION PROCESS

This application is a continuation-in-part of United States
Provisional Application Serial No. 60/000,747, filed June 30,
5   1995.

FIELD OF THE INVENTION

This invention concerns a process for the preparation of
polyolefins by coordination polymerization of ethylene, styrene or
norbornene by a nickel compound coordinated to a selected ligand.
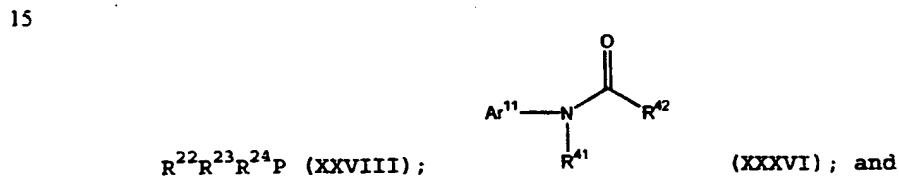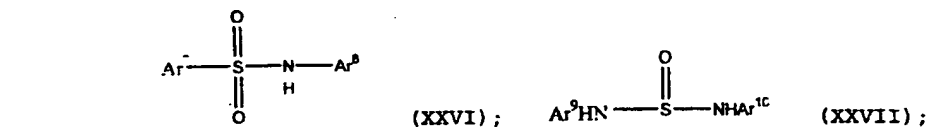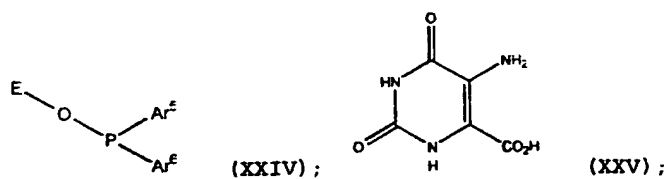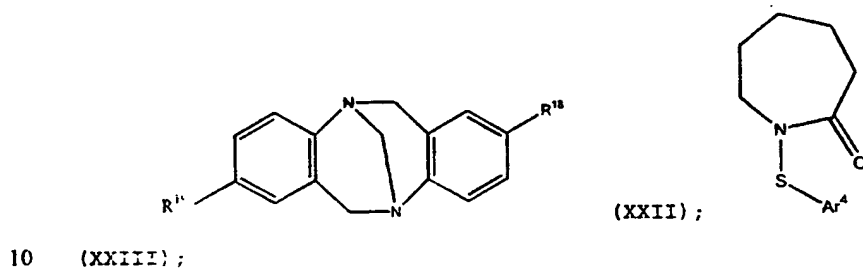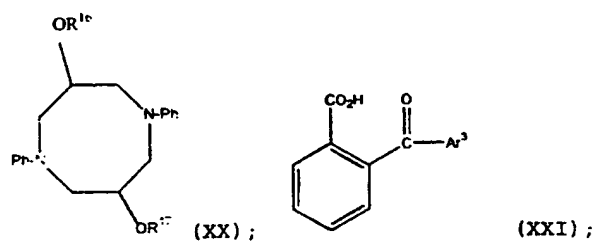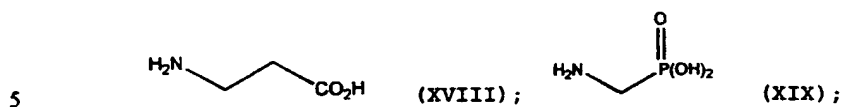
10   ### TECHNICAL BACKGROUND

Polyolefins are very important items of commerce, being used
for myriad uses, such as molding resins, films, ropes, composites,
fibers, elastomers, etc. Suitability for any particular use is
dependent on the polymer properties, for instance whether the
15   polymer is elastomeric or thermoplastic. One method of
polymerization of these olefins is by coordination polymerization,
use of a polymerization catalyst containing a transition metal,
the metal usually being thought of as coordinating to one or more
species during the polymerization process.

20   Whether any particular transition metal compound is an
olefin polymerization catalyst usually depends on the metal chosen
and what is coordinated (such as various ligands) to the metal
before and during the polymerization. Various transition metal
compounds may or may not be active catalysts for a particular
25   (type of) olefin, and the resulting polymer structures may vary.
Other factors such as the efficiency and rate of polymerization
may vary. Therefore, new transition metal catalysts for olefin
polymerizations are constantly being sought.

SUMMARY OF THE INVENTION

30   This invention concerns a process for the polymerization of
an olefin, comprising:

(a) contacting a polymerizable monomer consisting
essentially of ethylene, a norbornene or a styrene, and a catalyst
system comprising the product of mixing in solution a zerovalent
35   tricoordinate or tetracoordinate nickel compound (II) which has at
least one labile ligand, and all ligands are neutral, an acid of
the formula HX (IV), and a first compound selected from the group
consisting of:

Ar^{1}Q$_n$ (III);   R^{8}R^{10}N-CR^{4}R^5(CR^{6}R^7)$_m$-NR^{8}R^{10} (V);

(XVI);

(XVII);

(XVIII);

(XIX);

5

(XX);

(XXI);

(XXII);

(XXIII);

10

(XXIV);

(XXV);

(XXVI);

(XXVII);

15

R^{22}R^{23}R^{24}P (XXVIII);

(XXXVI); and

2

$$R^{\varepsilon}S-CR^4R^5(CR^6R^7)_m-SR^{\varepsilon} \quad (XXXVII);$$

wherein:

    X is a noncoordinating anion;

    Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

    each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

    n is 1 or 2;

    E is 2-thienyl or 2-furyl;

    each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

    each R^9 is independently hydrogen or hydrocarbyl; and

    each R^3 is independently a monovalent aromatic moiety;

    m is 1, 2 or 3;

    R^{43} is hydrogen or alkyl;

    each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

    each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

    each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

    Ar^2 is an aryl moiety;

    R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

    R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

    each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

    Ar^3 is an aryl moiety;

    R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

    Ar^4 is an aryl moiety;

    Ar^5 and Ar^6 are each independently hydrocarby;

    Ar^7 and Ar^8 are each independently an aryl moiety;

    Ar^9 and Ar^{10} are each independently an aryl moiety or $-CO_2R^{25}$, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

    Ar^{11} is an aryl moiety;

    R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or $-C(O)-NR^{41}-Ar^{11}$;

R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups

5   substituted by one or more alkoxy groups, each alkoxy group

containing 1 to 20 carbon atoms; and

        R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl

moiety.

        This invention also concerns a catalyst for the

10   polymerization of ethylene, a norbornene, or a styrene,

comprising, the product of mixing in solution a zerovalent

tricoordinate or tetracoordinate nickel compound (II) which has at

least one labile ligand and all ligands are neutral, an acid of

the formula HX (IV), and a compound selected from the group

15   consisting of:
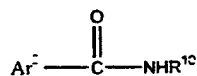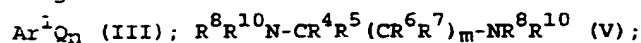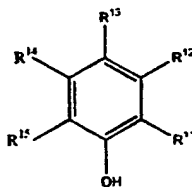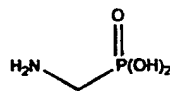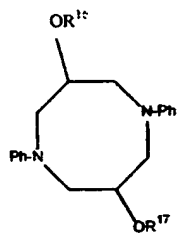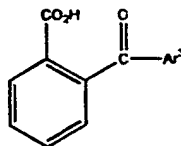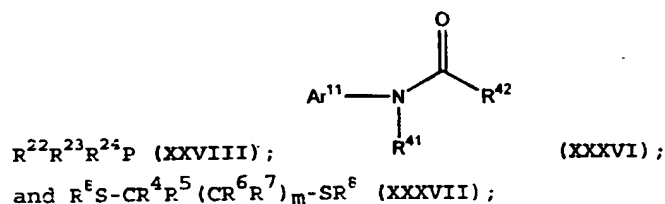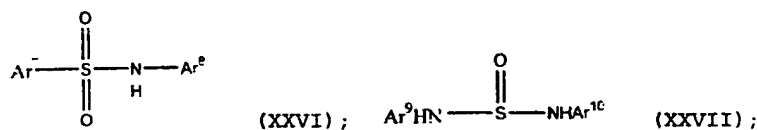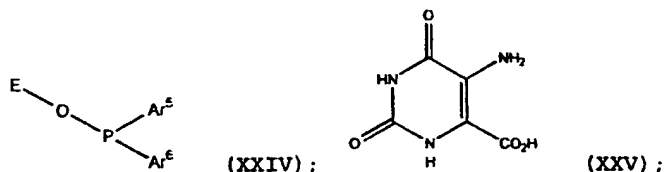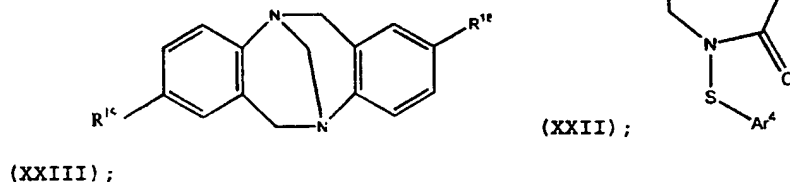
        $Ar^{1}Q_{n}$ (III); $R^{8}R^{10}N-CR^{4}R^{5}(CR^{6}R^{7})_{m}-NR^{8}R^{10}$ (V);

(XVI) ;   (XVII) ;

20   (XVIII) ;   (XIX) ;

            (XX) ;   (XXI) ;

(XXIII) ;

(XXII) ;

(XXIV) ;   (XXV) ;

(XXVI) ; Ar^9HN—S—$NHAr^{10}$ (XXVII) ;

$R^{22}R^{23}R^{24}P$ (XXVIII) ;   (XXXVI) ;

and $R^8S-CR^4R^5(CR^6R^7)_m-SR^8$ (XXXVII) ;

wherein:

X is a noncoordinating anion;

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

n is 1 or 2;

E is 2-thienyl or 2-furyl;

R^{43} is hydrogen or alkyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^3 is independently a monovalent aromatic moiety;

each R^9 is independently hydrogen or hydrocarbyl;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

5   Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is

10   about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or

15   hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety, -

20   CO_2R^{25}, or Ar^7 and Ar^8 taken together are a divalent aromatic moiety and wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or -C(O)-NR^{41}-Ar^{11};

25   R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

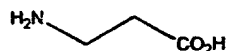R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl

30   moiety;

and provided that the molar ratio of (III), (V) (XVI), (XVII), (XVIII), (XIX), (XX), (XXI), (XXII), (XXIII), (XXIV), (XXV), (XXVI), (XXVII), (XXVIII), (XXXVI) or (XXXVII):(II) is about 0.5 to about 5, and the molar ratio of (IV):(II) is about

35   0.5 to about 10.

This invention also concerns a process for the polymerization of an olefin, comprising, contacting ethylene, a

norbornene, or a styrene with a nickel [II] complex of a ligand selected from the group consisting of:
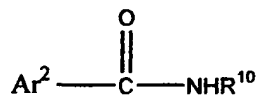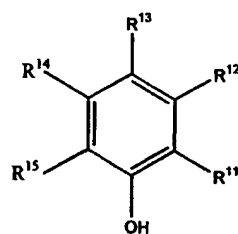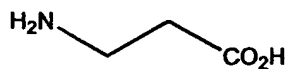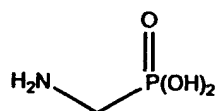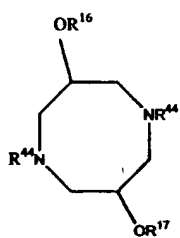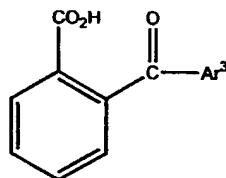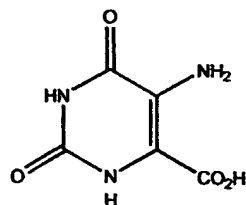
$$Ar^1Q_n \quad (III); \quad R^8R^{10}N-CR^4R^5(CR^6R^7)_m-NR^8R^{10} \quad (V);$$

5

$$Ar^2-\overset{O}{\underset{||}{C}}-NHR^{10} \quad (XVI);$$

(XVII);

$$H_2N \diagdown \diagup \diagdown_{CO_2H} \quad (XVIII);$$

$$H_2N \diagdown \overset{O}{\underset{||}{P(OH)_2}} \quad (XIX);$$

(XX);

(XXI);

10

(XXIII);

(XXII);

$$\overset{Ar^4}{\underset{S}{}}$$

15

$$E \diagdown O \diagdown \overset{Ar^5}{\underset{Ar^6}{P}} \quad (XXIV);$$

(XXV);

$$Ar^7-\overset{O}{\underset{O}{\overset{||}{\underset{||}{S}}}}-\overset{}{\underset{H}{N}}-Ar^8 \quad (XXVI); \quad Ar^9HN-\overset{O}{\underset{||}{S}}-NHAr^{10} \quad (XXVII);$$

7

SUBSTITUTE SHEET (RULE 26)

$$\text{Ar}^{11}\!-\!\!\overset{\displaystyle O}{\underset{\displaystyle\underset{R^{41}}{|}}{\overset{\|}{N}}}\!\!-\!\!\overset{\|}{C}\!\!-\!\!R^{42}$$
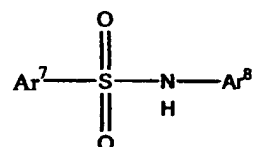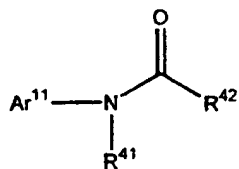
$R^{22}R^{23}R^{24}P$ (XXVIII);   (XXXVI);

and $R^8S\text{-}CR^4R^5(CR^6R^7)_m\text{-}SR^8$ (XXXVII);

wherein:

5   X is a noncoordinating anion;

           Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

           each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

           R^{43} is hydrogen or alkyl;

           n is 1 or 2;

10   E is 2-thienyl or 2-furyl;

           each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

           each R^3 is independently a monovalent aromatic moiety;

           each R^9 is independently hydrogen or hydrocarbyl; m is

15   1, 2 or 3;

           each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

           each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

20   each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

           Ar^2 is an aryl moiety;

           R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

25   R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

           each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

30   Ar^3 is an aryl moiety;

           R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

           Ar^4 is an aryl moiety;

           Ar^5 and Ar^6 are each independently hydrocarby;

35   Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^5 and Ar^{10} are each independently an aryl moiety, -CO_2R^{25}, or Ar^7 and Ar^6 taken together are a divalent aromatic moiety and wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

5   R^{41} is hydrogen or hydrocarbyl;

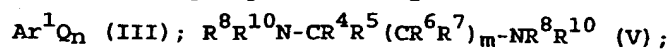R^{42} is hydrocarbyl or $-C(O)-NR^{41}-Ar^{11}$;

R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group

10   containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety.

Described herein is a process for the polymerization of olefins, comprising, contacting ethylene, a norbornene or a

15   styrene with a nickel containing first compound of the formula $[L^1_qL^2_rL^3_sL^4_tNi]^+X^-$ (XXXIII), wherein:

L^1 is a first monodentate neutral ligand coordinated to said nickel, L^2 is a second monodentate neutral ligand coordinated to said nickel which may be said first monodentate neutral ligand

20   and r is 0 or 1, or L^1 and L^2 taken together are a first bidentate neutral ligand coordinated to said nickel and r is 1;

L^3 and L^4 taken together are a π-allyl ligand coordinated to said nickel, L^3 and L^4 taken together are

25   (XXXII)
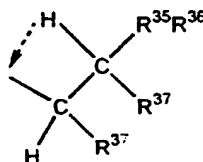
coordinated to said nickel, or L^3 is a third neutral monodentate ligand selected from the group consisting of ethylene, a norbornene and a styrene or a neutral monodentate ligand which can be displaced by an olefin, and L^4 is R^{38};

30   X is a relatively non-coordinating anion;

each of q, s and t is 1;

said first monodentate neutral ligand and said first bidentate neutral ligand are selected from the group consisting of Ar^1Q_n (III); $R^8R^{10}N-CR^4R^5(CR^6R^7)_m-NR^8R^{10}$ (V);

35

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(XVI);   (XVII);

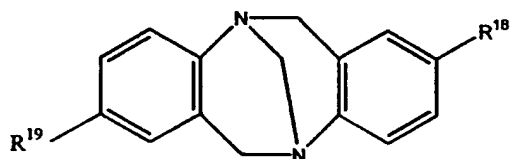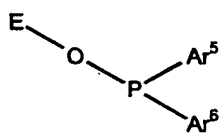(XVIII);   (XIX);
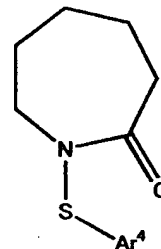
5   (XX);   (XXI);

(XXII);

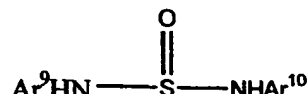(XXIII);

10   (XXIV);   (XXV);

(XXVI);   Ar^{9}HN—$\overset{\overset{\displaystyle O}{\|}}{S}$—NHAr^{10} (XXVII);

R^{22}R^{23}R^{24}P (XXVIII);   (XXXVI);

15   and R^{8}S-CR^{4}R^5(CR^{6}R^7)$_m$-SR^8 (XXXVII);

Ar^1 is an aromatic moiety with n free valencies, or
diphenylmethyl;

10

each Q is $-NR^2R^{42}$ or $-CR^9=NR^3$;

R^{43} is hydrogen or alkyl;

n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^9 is independently hydrogen or hydrocarbyl; and

each R^3 is independently a monovalent aromatic moiety;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety or $-CO_2R^{25}$, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or $-C(O)-NR^{41}-Ar^{11}$;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

11

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety;

R^{35} is hydrocarbylene;

R^{36} is hydrogen, alkyl, or $-C(O)R^{39}$;

each R^{37} is hydrocarbyl or both of R^{37} taken together are hydrocarbylene to form a carbocyclic ring;

R^{38} is hydride, alkyl or $-C(O)R^{39}$; and

R^{39} is hydrocarbyl

R^{44} is aryl.

Also described herein is a compound of the formula $[L^1_q L^2_r L^3_s L^4_t Ni]^+ X^-$ (XXXIII), wherein:

L^1 is a first monodentate neutral ligand coordinated to said nickel, L^2 is a second monodentate neutral ligand coordinated to said nickel which may be said first monodentate neutral ligand and r is 0 or 1, or L^1 and L^2 taken together are a first bidentate neutral ligand coordinated to said nickel and r is 1;

L^3 and L^4 taken together are a π-allyl ligand coordinated to said nickel, L^3 and L^4 taken together are

(XXXII)

coordinated to said nickel, or L^3 is a third neutral monodentate ligand selected from the group consisting of ethylene, a norbornene and a styrene or a neutral monodentate ligand which can be displaced by an olefin, and L^4 is R^{38};

X is a relatively non-coordinating anion;

q, s and t are each 1;

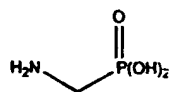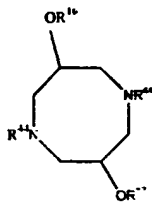said first monodentate neutral ligand and said first bidentate neutral ligand are selected from the group consisting of Ar^1Q_n (III); $R^8R^{10}N-CR^4R^5(CR^6R^7)_m-NR^8R^{10}$ (V);
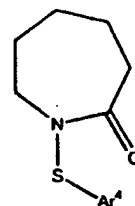
12

(XVI) ;

(XVII) ;

(XVIII) ;

(XIX) ;

5

(XX) ;

(XXI) ;

(XXII) ;

(XXIII) ;

10

(XXIV) ;

(XXV) ;

(XXVI) ;

(XXVII) ;

$R^{22}R^{23}R^{24}P$ (XXVIII) ;
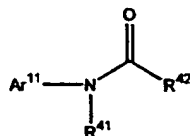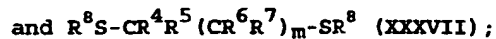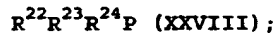
(XXXVI) ;

15   and R^8S-$CR^4R^5(CR^6R^7)_m$-SR^8 (XXXVII) ;

wherein:

13

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

R^{43} is hydrogen or alkyl;

n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^9 is independently hydrogen or hydrocarbyl; and

each R^3 is independently a monovalent aromatic moiety;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety or $-CO_2R^{25}$, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or $-C(O)-NR^{41}-Ar^{11}$;

R^{44} is aryl;

14

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl
5   moiety;

R^{35} is hydrocarbylene;

R^{36} is hydrogen, alkyl, or $-C(O)R^{39}$;

each R^{37} is hydrocarbyl or both of R^{37} taken together are hydrocarbylene to form a carbocyclic ring;
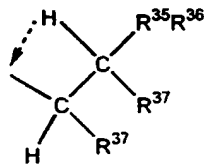10 R^{38} is hydride, alkyl or $-C(O)R^{39}$; and

R^{39} is hydrocarbyl.

Described herein is a compound of the formula
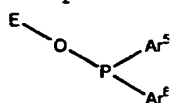
(XXIV)

15   wherein:

E is 2-thienyl or 2-furyl;

Ar^{5} and Ar^{6} are each independently hydrocarby.

DETAILS OF THE INVENTION

20   The olefins polymerized herein are ethylene, a styrene and a norbornene. Norbornene and styrene may be present in the same polymerization, and a copolymer may be produced. By a styrene herein is meant a compound of the formula
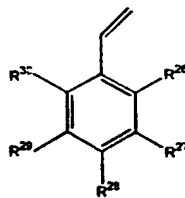
25   (XXIX)

wherein R^{26}, R^{27}, R^{28}, R^{29} and R^{30} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, all of which are inert in the polymerization process. It is preferred
30   that all of R^{26}, R^{27}, R^{28}, R^{29} and R^{30} are hydrogen.

By "a norbornene" is meant that the monomer is characterized by containing at least one norbornene-functional group in its

structure including norbornadiene as identified by the formulas

below, which can be substituted or unsubstituted

(XXXIV)
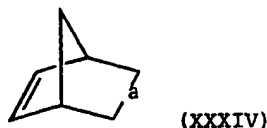
wherein "a" represents a single or double bond.

5   Representative monomers are compounds (XXXV) and (XXXX) as

follows:

(XXXIV);   (XXXX)

wherein R^{46}, R^{47}, R^{46}, and R^{49} independently are hydrogen halogen,

or hydrocarbyl, provided that, except if the hydrocarbyl group is

10   vinyl, if any of the hydrocarbyl are alkenyl, there is no terminal

double bond, i.e., the double bond is internal; or R^{46} and R^{48}

taken together can be part of carbocyclic ring (saturated,

unsaturated or aromatic); or R^{46} and R^{47} and/or R^{48} and R^{45} taken

together are an alkylidene group. In these structures "z" is 1 to

15   5.

     Examples of such norbornenes include norbornadiene, 2-

norbornene, 5-methyl-2-norbornene, 5-hexyl-2-norbornene, 5-

ethylidene-2-norbornene, vinylnorbornene, dicyclopentadiene,

dihydrodicyclopentadiene, tetracyclododecene, trimers of

20   cyclopentadiene, halogenated norbornenes wherein R^{46}, R^{47}, R^{48} and

R^{45} may also be halogen or fully halogenated alkyl groups such as

C_wF_{2w+1} wherein w is 1 to 20, such as perfluoromethyl and

perfluorodecyl.

     The halogenated norbornenes can be synthesized via the

25   Diels-Alder reaction of cyclopentadiene an appropriate

dieneophile, such as $F_3CC\equiv CCF_3$ or $R^{49}_2C=CR^{49}C_wF_{2w+1}$ wherein each R^{49}

is independently hydrogen or fluorine and w is 1 to 20.

It is also preferred that in the polymerization processes
described herein that the polymer produced has an average degree

5   of polymerization of about 10 or more, more preferably about 20 or
more, and especially preferably about 50 or more.

In the polymerization processes and catalyst compositions
described herein certain groups may be present. By hydrocarbyl is
meant a univalent radical containing only carbon and hydrogen. By

10   saturated hydrocarbyl is meant a univalent radical which contains
only carbon and hydrogen, and contains no carbon-carbon double
bonds, triple bonds and aromatic groups. By substituted
hydrocarbyl herein is meant a hydrocarbyl group which contains one
or more (types of) substitutents that does not interfere with the

15   operation of the polymerization catalyst system. Suitable
substituents include halo, ester, keto (oxo), amino, imino,
carboxyl, phosphite, phosphonite, phosphine, phosphinite,
thioether, amide, nitrile, and ether. Preferred substituents are
halo, ester, amino, imino, carboxyl, phosphite, phosphonite,

20   phosphine, phosphinite, thioether, and amide. By benzyl is meant
the $C_6H_5CH_2-$ radical, and substituted benzyl is a radical in which
one or more of the hydrogen atoms is replaced by a substituent
group (which may include hydrocarbyl). By phenyl is meant the
C_6H_5- radical, and a phenyl moiety or substituted phenyl is a

25   radical in which one or more of the hydrogen atoms is replaced by
a substituent group (which may include hydrocarbyl). Preferred
substituents for substituted benzyl and phenyl include those
listed above for substituted hydrocarbyl, plus hydrocarbyl. If
not otherwise stated, hydrocarbyl, substituted hydrocarbyl and all

30   other groups containing carbon atoms, such as alkyl, preferably
contain 1 to 20 carbon atoms.

By an aromatic moiety herein is meant a radical containing
at least one carbocyclic or heterocyclic aromatic ring, which has
a number of free valences to the carbon atoms of the aromatic

35   carbocyclic ring(s). A monovalent aromatic moiety has one free
valence, and herein is termed an aryl moiety. If there is more
than one aromatic ring in the radical, the ring may be joined by
covalent bonds (as in biphenyl) or may be fused (as in

17

naphthalene), or both. The free valencies may be at carbon atoms in one ring, or more than one ring if more than one ring is present. The aromatic ring(s) may be substituted by hydrocarbyl groups or other substitutents which don't interfere with the

5   catalytic activity of the catalyst system. Substituents that aid the polymerization may be present. Suitable and preferred substituents are as listed above for substituted hydrocarbyl groups. Suitable aromatic radicals herein include phenyl, o-phenylene, 1,8-naphthylene, and 2-thiophenyl.

10   A transition metal compound which may be initially added to a polymerization process mixture is (II), a zerovalent nickel compound which is tricoordinate or tetracoordinate. Also included within the definition of this zerovalent nickel compound are mixtures of compounds which will generate suitable zerovalent

15   nickel compounds in situ, such as mixtures of nickel compounds in higher valence states with suitable reducing agents. The ligands which are coordinated to the nickel atom may be monodentate or polydentate, so long as the nickel compound is tricoordinate or tetracoordinate. The ligands should be such that at least two,

20   and preferably all, of the coordination sites of the nickel atom are coordinated to ligands which are readily, reversibly or irreversibly, displaceable by (III),(V), or any one of (XVI) to (XIX), (XXXVI) and (XXXVII). Such readily displaceable ligands include η^4-1,5-cyclooctadiene and tris(o-tolyl)phosphite (which is

25   a phosphite with a large cone angle), ethylene and carbon monoxide. A preferred nickel compound (II) is bis(η^4-1,5-cyclooctadiene)nickel[0].

       By the compound HX is meant the acid of a noncoordinating monoanion, or the equivalent thereof, i.e., a combination of

30   compounds that will generate this acid. Noncoordinating anions are well known to the artisan, see for instance W. Beck., et al., Chem. Rev., vol. 88, p. 1405-1421 (1988), and S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993), both of which are hereby included by reference. Relative coordinating abilities of such

35   noncoordinating anions are described in these references, Beck at p. 1411, and Strauss at p. 932, Table III. Also useful in this process in place of HX are "solid" acids, such as acidic aluminas,

clays and zirconias, which are considered herein to be acids with relatively non-coordinating anions.

Preferred anions X are BF_4^-, PF_6^-, and BAF {tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, SbF^-, and BAF is especially

5   preferred. The acids of these anions are known, for instance HBF_4 is commercially available, and HBAF can be made by the method described in M. Brookhart, et al., Organometallics, vol. 11, p. 3920-3922 (1992).

In all forms of (III) it is preferred that R^9 and R^{43} are

10   hydrogen. If R^{43} is alkyl, it is preferred that it is methyl. In all forms of (III), each R^2 may be independently hydrogen, hydrocarbyl or substituted hydrocarbyl, and it is preferred that each R^2 is hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl.

15   In one preferred form of (III), n is 1 and Q is $-NR^2R^{43}$. It is preferred that R^2 is hydrogen and that Ar^1 is 2,6-dialkylphenyl or amide, carboxy, or keto substituted phenyl. More preferably, Ar^1 is 2,6-diisopropylphenyl, 2-carbomoylphenyl, 2-carboxyphenyl, or 2-benzoylphenyl.

20   In another preferred form of (III), n is 2 and each Q is $-NR^2R^{43}$. In this instance it is more preferred that R^2 is hydrogen, and/or Ar^1 is o-phenylene or 1,8-naphthylene, and it is especially preferred that Ar^1 is 1,8-naphthylene.

In (III), when n is 1 and Q is $-CR^9=NR^3$, it is preferred

25   that R^9 is hydrogen, and R^3 is preferably 2,6-dialkylphenyl, or amide, ester, carboxyl, keto, or halo substituted phenyl. More preferably, R^3 is 2,6-diisopropylphenyl, 2-carbomoylphenyl, 2-carbomethoxyphenyl, 2-carboxyphenyl, 1-fluoren-9-onyl, 1-anthraquinolyl, or pentafluorophenyl. Ar^1 is aryl, or halo,

30   ester, amino, imino, carboxyl, phosphite, phosphonite, phosphine, phosphinite, ether, thioether, or amide substituted phenyl. More preferably, Ar^1 is diphenylmethyl, 9-anthracenyl, 2-furanyl, 2-thiofuranyl, 2-phenolyl, or 2-hydroxy-naphthyl. When Ar^1 is diphenylmethyl, these tautomeric forms are believed to exist when

35   these compounds are complexed to nickel.

When in (III) n is 2 and Q is $-CR^9=NR^3$, it is preferred that Ar^1 is p-phenylene, and that R^3 is 2,6-disubstituted phenyl in which the substitutents are halo, alkyl, or halo and alkyl.

19

In (III), when Q is $-NHR^2$, R^2 taken together with Ar^1 may form a carbocyclic or heterocyclic ring, as long as the atom of R^2 attached directly to the nitrogen atom is a saturated carbon atom. Thus another preferred compound (III) is
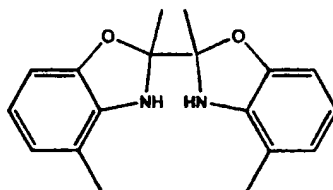
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It will be noted that there are actually two amino groups in this compound that meet the criteria for Q. This is compound **105**, below.

For (V) it is preferred that m is 1, all of R^4, R^5, R^6, R^7

10   and R^{10} are hydrogen, and both of R^8 are 2,6-dialkylphenyl, especially 2,6-diisopropylphenyl, or cyclohexyl. In another preferred compound (V) m is 1, all of R^4, R^5, R^6, and R^7 are hydrogen, both of R^8 are phenyl, and both of R^{10} are ethyl. In (V) too much or too little steric hindrance around the nitrogen

15   atoms may cause a catalytic composition containing such a compound to be ineffective as an olefin polymerization catalyst.

In (XVI) is preferred that Ar^2 is phenyl, 2-pyridyl, or 3-hydroxyl-2-pyridyl, and/or R^{10} is hydrogen, phenyl, 2,6-diisopropylphenyl,1-naphthyl, 2-methyl-1-naphthyl, or 2-

20   phenylphenyl.

In (XVII) it is preferred that R^{12} and R^{14} are hydrogen, and/or R^{13} is hydrogen or t-butyl, and/or R^{11} and R^{15} are both t-butyl or both phenyl, and/or R^{11} is t-butyl and R^{15} is 2-hydroxy-3,5-di-t-butylphenyl. Note that when R^{15} is 2-hydroxy-3,5-di-t-

25   butylphenyl the compound contains 2 phenolic hydroxy groups, both of which are sterically hindered.

The steric effect of various groupings has been quantified by a parameter called E_s, see R. W. Taft, Jr., J. Am. Chem. Soc., vol. 74, p. 3120-3128 (1952), and M.S. Newman, Steric Effects in

30   Organic Chemistry, John Wiley & Sons, New York, 1956, p. 598-603. For the purposes herein, the E_s values are those described in these publications. If the value for E_s for any particular group is not known, it can be determined by methods described in these publications. For the purposes herein, the value of hydrogen is

35   defined to be the same as for methyl. It is preferred that the

20

total E_s value for the ortho (or other substituents closely
adjacent to the -OH group) substitutents in the ring be about -1.5
or less, more preferably about -3.0 or less. Thus in a compound
such as 2,4,6-tri-t-butylphenol only the E_s values for the 2 and 6
5 substituted t-butyl groups would be applicable.

In (XX) it is preferred that both R^{16} and R^{17} are hydrogen or
that both are acyl. A preferred acyl group is $CH_3C(O)-$.

In (XXI) it is preferred that Ar^3 is phenyl or substituted
phenyl, more preferably phenyl.

10 In (XXII) it is preferred that both of R^{18} and R^{19} are
methyl, or both are hydrogen.

In (XXIII) it is preferred that Ar^4 is phenyl or substituted
phenyl, more preferably phenyl.

In (XXIV) it is preferred that Ar^5 and Ar^6 are independently

15 phenyl, substituted phenyl, or cyclohexyl, and it is especially

preferred when both are cyclohexyl or both are phenyl.

In (XXVI) it is preferred that Ar^7 and Ar^8 are independently
phenyl or substituted phenyl. In a specific preferred compound,
20 Ar^7 is phenyl or p-tolyl and Ar^8 is 2,6-diisopropylphenyl.

In (XXVII) it is preferred that R^{25} is methyl. Specific
preferred compounds are
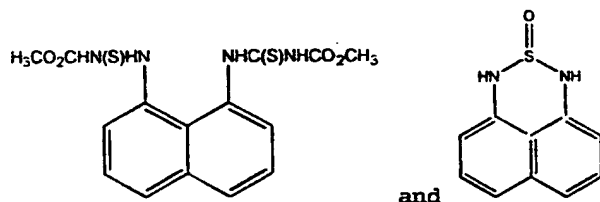
25 Note that in one of these compounds there are 2 thiourea groups
present.

In (XXVIII) it is preferred that R^{22}, R^{23} and R^{24} are each
independently o-tolyl, 2,4,6-trimethoxyphenyl, 2,6-
dimethoxyphenyl, 2-methoxyphenyl, and 2,3,6-trimethoxyphenyl.
30 Other preferred groups for R^{24} are ethyl, isopropyl and phenyl.
It is also preferred that R^{24} is an aryl moiety. In another
preferred form, when R^{22}, R^{23} and/or R^{24} are phenyl or substituted
phenyl, there is at least one alkoxy group, preferably a methoxy

21

group, ortho (in the benzene ring) to the phosphorous atom.
Another compound (XXVIII) is 1,3-bis[(bis-2,6-
dimethoxyphenyl)phosphino]propane. This compound actually has two
phosphine groups that each structurally meet the requirements for

5   a compound of type (XXVIII).

It is also preferred that each of R^{22}, R^{23}, and R^{24} (when it
is an aryl moiety) contain electron donating groups bound to the
aromatic moiety through a carbon atom of an aromatic ring. The
concept of electron donating groups is well known to the artisan.

10   One method of measuring the electron donating ability of a group
(particularly in a benzene ring, but it is not limited to such
rings) which is not adjacent to the "active" center is by using
the Hammett equation, see for instance H. H. Jaffe, Chem. Rev.,
vol. 53, p. 191-261 (1953). The actual result of this is called

15   the Hammett σ constant. For ortho (adjacent) substituents one may
use the Taft σ* constant as determined by measurements on ortho-
benzoate esters, see for instance R. W. Taft, Jr., J. Am. Chem.
Soc., vol. 74, p. 3120-3128 (1952); ibid., vol. 75, p. 4231-4238
(1953); and C. K. Ingold, Structure and Mechanism in Organic

20   Chemistry, 2nd Ed., Cornell University Press, Ithaca, 1969, p.
1220-1226. It is preferred that the total of the σ and σ*
constants for any of the groups R^{22}, R^{23}, and R^{24} (when it is an
aryl moiety) be about -0.25 or less, more preferably about -0.50
or less (it is noted that the σ and σ* constants for electron

25   donating groups are negative, so the more electron donating groups
present, the more negative this total becomes) and especially
preferably about -0.75 or less.

In (XXXVI) it is preferred that Ar^{11} is 2,6-dialkylphenyl,
more preferably 2,6-dimethylphenyl or 2,6-diisopropylphenyl It is

30   preferred that R^{42} is -C(O)-NR^{41}-Ar^{11}. It is preferred that R^{41} is
hydrogen.

In (XXXVII) it is preferred that m is 1, and/or all of R^4,
R^5, R^6 and R^7 are hydrogen, and/or both of R^8 are aryl moieties,
more preferably both of R^8 are 2,6-dialkylphenyl, and especially

35   preferably both of R^8 are 2,6-dimethylphenyl.

In some of the compounds herein, the group -$CHPh_2$,
diphenylmethyl, may appear, especially when the methine carbon
atom can be bound to the carbon atom of an imine. In this case

one can write such a compound as -N=CH-CHPh$_2$ (the imine form) or as
-NH-CH=CPh$_2$ (amine form). It has been found that in the free
compounds (not complexed to nickel) this group is usually in the
amine form. However, in a few of the nickel complexes of these

5   types of compounds the preliminary evidence indicates the ligand
is present in the imine form. Therefore, one may consider these
forms interchangeable for the purposes herein, and it is noted
that both types of compounds are mentioned in the claims herein.

The ligands can be made by methods that can be readily found

10 in the literature, and/or are available commercially or form
laboratory supply houses, or are described in the Examples herein.

The polymerization may also be carried out by
$[L^1_qL^2_rL^3_sL^4_tNi]^+X^-$ (XXXIII), which may be formed in situ or added
directly to the initial polymerization mixture. For example,

15 (XXXIII) may be in the form of a π-allyl complex. By a π-allyl
group is meant a monoanionic radical with 3 adjacent sp^2 carbon
atoms bound to a metal center in an η^3 fashion. The three sp^2
carbon atoms may be substituted with other hydrocarbyl groups or
functional groups. Typical π-allyl groups include

20

wherein R is hydrocarbyl. In (XXXIII) when it is a π-allyl type
complex, L^3 and L^4 taken together are the π-allyl group. As shown

25 in many of the Examples herein, these π-allyl compounds may be
stable, and may be used themselves to initiate the olefin
polymerization.

Initiation with π-allyl compounds may be sluggish at times.
Initiation of π-allyl compounds can be improved by using one or

30 more of the following methods:

● Using a higher temperature such as about 80°C.

● Decreasing the bulk of the ligand, such as R^2 and R^5
being 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl.

● Making the π-allyl ligand more bulky, such as using

35

rather than the simple π-allyl group itself.

•   Having a Lewis acid present while using a functional
π-allyl. Relatively weak Lewis acids such a triphenylborane,
tris(pentafluorophenyl)borane, and tris(3,5-
trifluoromethylphenyl)borane, are preferred. Suitable functional
groups include chloro and ester. "Solid" acids such as
montmorillonite may also be used.

However, (XXXIII) may also be present in the polymerization
in other "forms". For instance, L^3 may be an olefin, such as
ethylene, a norbornene or a styrene or a ligand capable of being
displaced by an olefin. By a ligand capable of being displaced by
an olefin is meant that the ligand is more weakly coordinating to
nickel than an olefin, and when in the complex is in contact with
an olefin, the olefin displaces it. Such ligands are known in the
art and include dialkyl ethers, tetrahydrofuran and nitriles such
as acetonitrile.

When L^3 is an olefin, L^4 may be $-R^{35}R^{36}$. R^{35} is alkylene,
but it actually is a "polymeric" fragment with one or more repeat
units (derived from the olefin(s) being polymerized) making up
R^{35}. In this form (XXXIII) may be said to be a living ended
polymer, further polymerization adding more repeat units to R^{35}.
R^{36} may be thought of as the end group of the polymeric group R^{35},
and may be derived from the similar grouping such as R^{38} which was
originally coordinated to the nickel.

When L^3 and L^4 in (XXXIII) taken together are (XXXII),
(XXXIII) may also be thought of as a living polymer. This type of
grouping is often referred to as an "agostic" coordination, and in
this group $-R^{35}R^{36}$ may be thought of in the same way as described
above. Whether a living ended molecule will be in a form with a
coordinated olefin or contain (XXXII) will depend on the other
ligands coordinated to nickel, and the nature of the olefin being
polymerized. It is believed that cyclic olefins tend to have
living ends containing agostic groupings.

In (XXXIII) it is preferred that r is 1. The second
monodentate neutral ligand may be any ligand which fits this
description, including being the same as the first neutral
monodentate ligand. Oftentimes though this ligand is a dialkyl

ether such as diethyl ether or an aliphatic nitrile such as
acetonitrile, or tetrahydrofuran. By "neutral" in the context of
(XXXIII) is meant that the ligand is electrically neutral, i.e.,
is not charged. In (XXXIII) preferred structures for the first
5   neutral monodentate ligand are those shown above. However, in
certain circumstances, L^1 and L^2 may be a single neutral bidentate
ligand of the same formula as when L^1 is a neutral monodentate
ligand. In other words, some of the compounds (III), (V), (XVI)
to (XXVIII), (XXXVI) and (XXXVII) may act as bidentate ligands in
10   (XXXIII). This may depend on the ligand itself, what the ratio of
ligand to Ni is, what the other ligands may be, and whether there
are any other compounds present which may also act as ligands.

When r in (XXXIII) is zero, simple dimers (containing 2 Ni
atoms) with bridging ligands of the compound $[L^1L^3L^4Ni]^+X^-$ are
15   also included within the definition of (XXXIII). For instance a
dimer containing L^1, r is zero, and L^3 and L^4 are combined into an
π-allyl group could have the formula
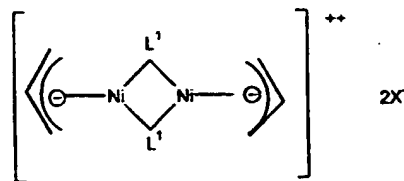
In this structure both L^1 ligands are bridging between the 2
20   nickel atoms. This type of dimer is familiar to those skilled in
the art, and is believed to readily disassociate into "monomeric"
nickel compounds on exposure to olefin.

Some of the forms of (XXXIII) are relatively unstable, and
are difficult to isolate as pure compounds. Nevertheless their
25   presence can be demonstrated by various methods known in the art.
For instance, "living end" and other forms of (XXXIII) may be
detected in solution by nuclear magnetic resonance (NMR) analysis,
especially a combination of ^1H and ^{13}C NMR. Such detection of
living ends is usually best done when R^{35} contains relatively few
30   repeat units.

(XXXIII) may be made by methods described herein, especially
in the Examples, or may actually be formed in situ at the
beginning of or during the polymerization process. It is believed
that when (III), (V), (XVI) to (XXVIII), (XXXVI) or (XXXVII), and

(II) and HX are mixed together in solution a coordination compound
such as (XXXIII) is formed which is active as a catalyst for the
polymerization of olefins.

5   The preparation of one of the catalyst systems, when (II) is
used, may be carried out in solution. By solution is meant that
(II) and (III), (V), (XVI) to (XIX), (XXXVI) or (XXXVII), and (IV)
are at least initially somewhat soluble in the solvent chosen. By
somewhat soluble is meant that at least a 0.01 molar solution of
each of the components in the solvent may be formed under process
10   conditions. This catalyst system may them be removed from the
solvent, as by evaporation of the solvent under vacuum, and then
contacted with one or more olefins to carry out the
polymerization. However, it is preferred to carry out the
polymerization in the presence of the "original" solvent in which
15   the active catalyst is formed. One or more of the components,
including the polymer product, may become insoluble as the
polymerization proceeds. Useful solvents include hydrocarbons
such as toluene or benzene. Benzene is a preferred solvent. The
benzene used herein is benzene-d$_6$.

20   Although it is not critical, when (II) is present it is
preferred that the molar ratio of (III), (V), (XVI) to (XXVIII),
(XXXVI) or (XXXVII):(II) is about 0.5 to 5, and the molar ratio of
(IV):(II) is about 0.5 to about 10. It is also preferred that all
the polymerizations be carried out at a temperature of about
25   -100°C to about +200°C, more preferably about -20°C to about
+100°C.

The polymers produced by this process are useful as molding
resins, films and elastomers.

Most of the formulas for (III), (V), (XVI) to (XXVIII),
30   (XXXVI) and (XXXVII) are generic formulas and embrace a wide range
of actual compounds. The ability of such individual compounds to
form active polymerizations catalysts, and the actual activity of
those catalysts, will be dependent on the structure of the
individual compound used, and the circumstances under which it is
35   used. For instance, whether such a compound will be active and
how active it will be will be dependent to some extent on its
actual structure, and particularly how that structure affects the
steric and electronic properties of the compound as a ligand on

nickel. If there is too much or too little steric hindrance about the group that actually coordinates to the nickel atom, the compound may be ineffective. Similarly, if the group that actually coordinates to the nickel is made too electron rich or poor, the compound may be made ineffective.

This may be illustrated by the following list of compounds, which were ineffective in catalyzing the polymerization of ethylene under the conditions described for Examples 23-66. The specific compounds are:
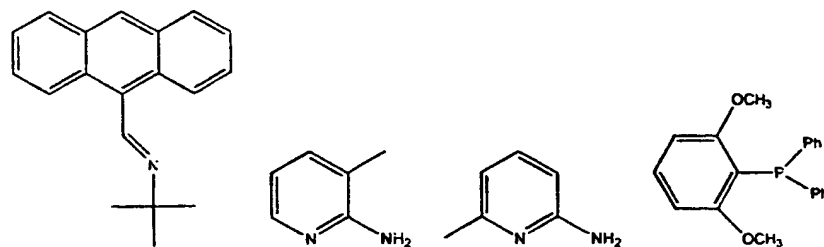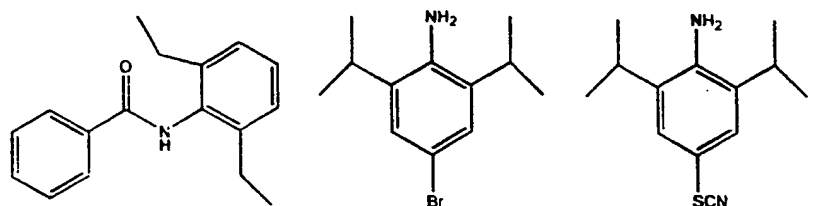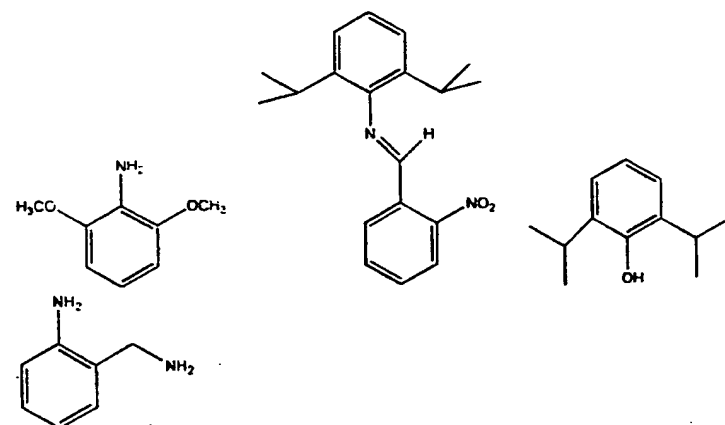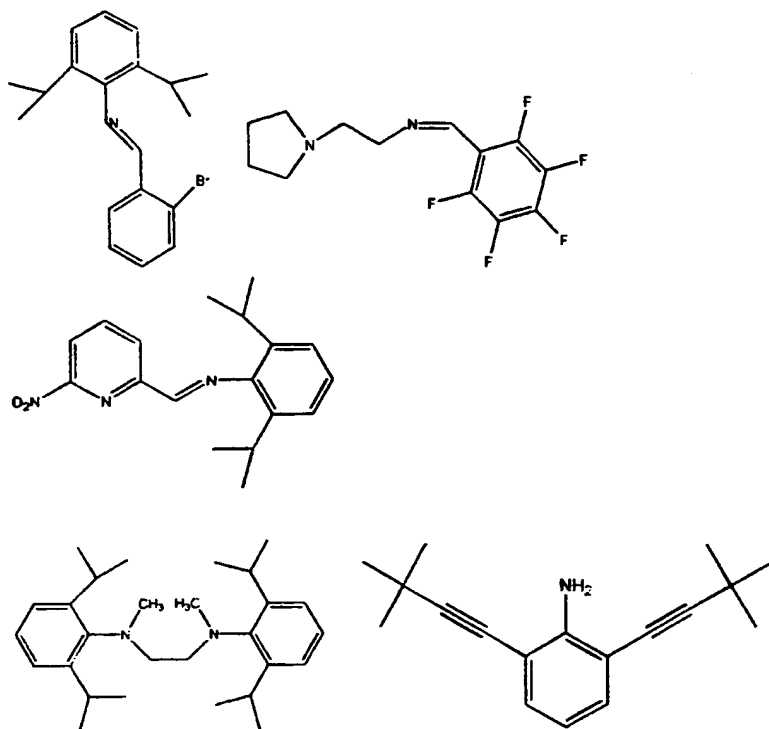
However, as mentioned above these compounds failed under a
specific set of conditions. If one peruses through the Examples
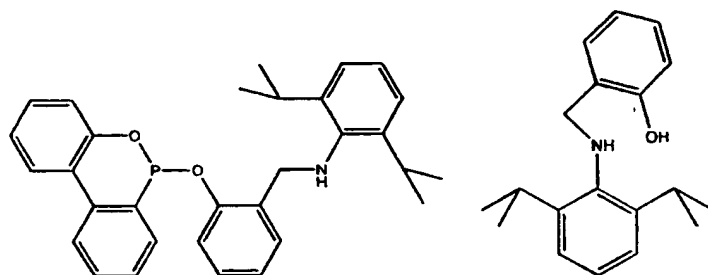herein, one will find that certain of these compounds may fail to
promote polymerization by one method, while be active in another

28

method, and/or one finds the yield of polymer may change significantly under different conditions. Therefore failure in any particular polymerization process doesn't mean failure in all.

Conditions in such processes may be varied, for instance the
5   pressure, temperature and solvent used. The polymerizations may be carried out in slurry, solution or the gas phase, in continuous, semi-batch or batch reactors. In addition, the particular starting form of the (proto)catalyst system may affect reactivity. For instance, differences may be found when using
10   (II) as a starting material than when using a preformed π-allyl complex.

Determining the activity of any particular compound which is described herein is relatively easy. The compound may be used in any of the polymerization systems described herein, and if needed
15   the conditions, such as temperature and pressure, may be varied. Particularly for polymerizations in which the active nickel catalyst is formed in situ, it may be important that the catalyst components all be soluble, at least initially, so solvent selection may be important. Such experiments are simple and quick
20   to run and don't involve much experimentation.

It is also noted that some forms of (XXXIII) may be prepared by other methods known in the art, see for instance copending U.S. Application Number 08/590,650, filed January 24, 1996 (CR9608D) which is hereby included by reference.
25   In all of the polymerization processes and polymerization catalysts herein it is preferred that one or more of the following not be significantly present: an organoaluminum compound; an aluminum halide; any other transition metals, especially titanium and/or zirconium; reducing agents, especially metal or metalloid
30   hydrides; and any organometalic compound except for nickel compounds. By not significantly present is meant there is not enough present to affect the course of the polymerization. It is more preferred that one or more of these be absent from a polymerization process and/or polymerization catalyst, except for
35   normal impurities. It is also preferred that a polymerization catalyst or catalyst system for a polymerization process herein consist essentially of the stated ingredients.

In all of the nickel complexes herein, except those specifically enumerated as nickel [0] complexes, it is preferred that the nickel be in the +2 oxidation state.

In the Examples the following abbreviations are used:

5   BAF - {tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}

        Bu - butyl

        COD - η^4-1,5-cyclooctadiene

        Cy - cyclohexyl

        DSC - differential scanning calorimetry

10   Et- ethyl

        Me - methyl

        Ph - phenyl (C_6H_5-)

        RT - room temperature

        Tg - glass transition temperature

15   THF - tetrahydrofuran

        TLC - thin layer chromatography

        Tm - melting point

In the Examples, all ethylene pressures are gauge pressures unless otherwise noted. The formulas given for the nickel

20 complexes of specific ligands in the Examples may not be accurate and are for illustration purposes only. They represent the best estimate of the structure (or one of several possible structures) based on available data.

Example 1

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and compound (VI) (0.023 g, 0.06 mmol) (purchased from the SALOR fine chemical division of Aldrich Chemical Co.) were dissolved in

5   benzene (5.0 mL). To the resulting solution was added HBAF'(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction

10 mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture contained polyethylene, which was washed with methanol and dried; yield of polymer = 9.1 g. ^{1}H NMR (CDCl$_2$CDCl$_2$, 120°C) showed that this sample contained 90 methyl-ended branches per 1000 methylenes. Two melting points were

15 observed by differential scanning calorimetry: a very broad melting point centered at approximately 0°C, and a sharp melting point at 115°C.
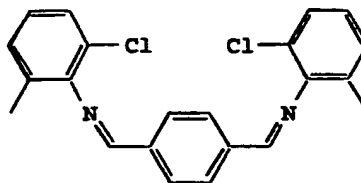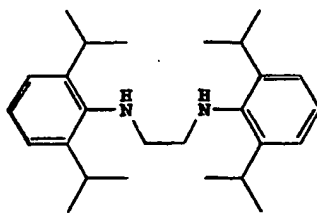

(VI)

20   ## Example 2

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and compound (VII) (0.023 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF'(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen

25 inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture contained polyethylene, which was filtered off, washed with

30 methanol and dried; yield of polymer = 4.9 g. By ^{1}H NMR integration it was shown that this material was branched polyethylene containing 109 methyl-ended branches per 1000 methylenes. ^{1}H NMR (CDCl$_3$) d 1.24 (s, methylene and methine protons), 0.82 (d, methyls).
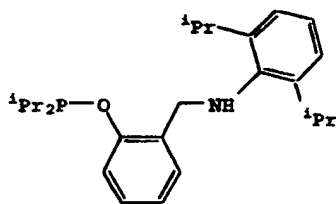
35

(VII)

Example 3

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)

5   and compound (VIII) (0.024 g, 0.06 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF'(Et$_2$O)$_2$ (0.060
g, 0.06 mmol). The resulting solution was immediately frozen
inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw

10   under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture
contained polyethylene, which was filtered off, washed with
methanol and dried; yield of polymer = 0.26 g. ^{1}H NMR (C$_6$D$_3$Cl$_3$,
120°C) showed that this sample contained 18 methyl-ended branches
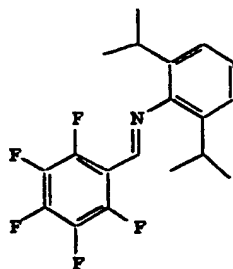
15   per 1000 methylenes.

(VIII)

Example 4

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)

20   and compound (IX) (0.020 g, 0.06 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF'(Et$_2$O)$_2$ (0.060
g, 0.06 mmol). The resulting solution was immediately frozen
inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw

25   under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture
contained polyethylene, which was washed with methanol and dried;
yield of polymer = 0.73 g. T_m = 126.9°C (second heat) as
determined by DSC. ^{1}H NMR (CDCl$_2$CDCl$_2$, 25°C) showed that this

sample contained approximately 7 methyl-ended branches per 1000
methylenes.

(IX)

Example 5

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and compound (X) (0.030 g, 0.06 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF˙(Et$_2$O)$_2$ (0.060
g, 0.06 mmol). The resulting solution was immediately frozen
inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw
under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture
contained polyethylene, which was washed with methanol and dried;
yield of polymer = 1.40 g. T$_m$ = 123.6°C as determined by DSC. ^{1}H
NMR (CDCl$_2$CDCl$_2$, 120°C) showed that this sample contained
approximately 10 methyl-ended branches per 1000 methylenes.
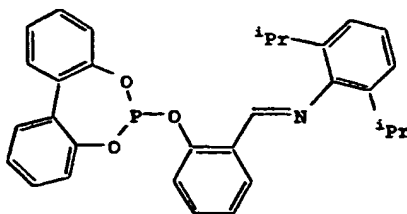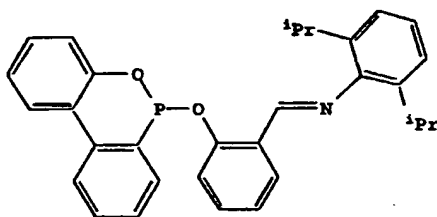

(X)

Example 6

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and compound (XI) (0.029 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060

5   g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture

10 contained polyethylene, which was filtered off, washed with methanol and dried; yield of polymer = 0.43 g. ^{1}H NMR (CDCl$_2$CDCl$_2$, 120°C) showed that this sample contained 19 methyl-ended branches per 1000 methylenes.

15   (XI)

Example 7

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and 2,6-diisopropylaniline (0.011 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added

20 HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The

25 final reaction mixture contained polyethylene, which was filtered off, washed with methanol and dried; yield of polymer = 0.72 g. T_m = 121.3°C (second heat) as determined by DSC. ^{1}H NMR (C$_6$D$_3$Cl$_3$, 120°C) showed that this sample contained 26 methyl-ended branches per 1000 methylenes. Another experiment run under identical

30 conditions afforded 0.17 g of polymer; three other experiments in which 0.12 mmol of 2,6-diisopropylaniline were employed (other conditions the same as above) afforded 0.30 g, 0.20 g, and 0.64 g of polymer.

Example 8

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and 2,6-diethylaniline (0.018 g, 0.12 mmol) were dissolved in
benzene (5.0 mL). To the resulting solution was added

5. HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was
immediately frozen inside a 40 mL shaker tube glass insert. The
glass insert was transferred to a shaker tube, and its contents
allowed to thaw under an ethylene atmosphere. The reaction
mixture was agitated under 6.9 MPa C$_2$H$_4$ for 14 h at 25°C. The

10 final reaction mixture contained polyethylene, which was filtered
off, washed with methanol and dried; yield of polymer = 0.34 g.
T$_m$ = 122.5°C (second heat) as determined by DSC.

Example 9

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)

15 and aniline (0.011 g, 0.12 mmol) were dissolved in benzene (5.0
mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060 g,
0.06 mmol). The resulting solution was immediately frozen inside
a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw

20 under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 14 h at 25°C. The final reaction mixture
contained polyethylene, which was filtered off, washed with
methanol and dried; yield of polymer = 0.049 g. T$_m$ = 112.0°C as
determined by differential scanning calorimetry.
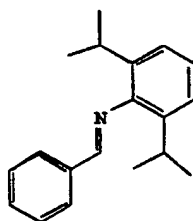
25 ### Example 10

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and 1,8-diaminonaphthalene (0.010 g, 0.06 mmol) were dissolved in
benzene (5.0 mL). To the resulting solution was added
HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was

30 immediately frozen inside a 40 mL shaker tube glass insert. The
glass insert was transferred to a shaker tube, and its contents
allowed to thaw under an ethylene atmosphere. The reaction
mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The
final reaction mixture contained polyethylene, which was washed

35 with methanol and dried; yield of polymer = 5.38 g. DSC on this
sample showed a very broad melting point, T$_m$ = 37.0°C (second
heat).

Example 11

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and compound (XII) (0.016 g, 0.12 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060

5   g, 0.06 mmol). The resulting solution was immediately frozen
inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw
under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h; during this time the temperature

10   inside the reactor varied between 25 and 33°C . The final
reaction mixture contained polyethylene, which was filtered off,
washed with methanol and dried; yield of polymer = 0.13 g. T$_m$ =
119.3, 129.0°C as determined by DSC.

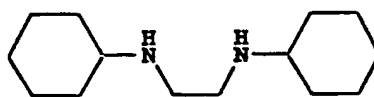
15   (XII)

Example 12

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and ortho-phenylenediamine (0.013 g, 0.12 mmol) were dissolved in
benzene (5.0 mL). To the resulting solution was added

20   HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was
immediately frozen inside a 40 mL shaker tube glass insert. The
glass insert was transferred to a shaker tube, and its contents
allowed to thaw under an ethylene atmosphere. The reaction
mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The

25   final reaction mixture contained polyethylene, which was filtered
off, washed with methanol and dried; yield of polymer = 0.052 g.
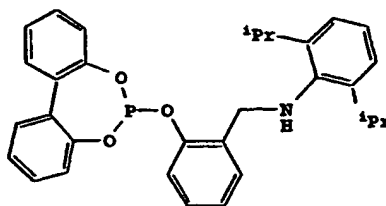T$_m$ = 98.0, 119.0°C as determined by DSC.

Example 13

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and compound (XIII) (0.013 g, 0.06 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060

5   g, 0.06 mmol). The resulting solution was immediately frozen
inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw
under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h at 25°C. The final reaction mixture

10 contained polyethylene, which was filtered off, washed with
methanol and dried; yield of polymer = 0.76 g.

(XIII)

15   Example 14

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and compound (XIV) (0.030 g, 0.06 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060
g, 0.06 mmol). The resulting solution was immediately frozen

20 inside a 40 mL shaker tube glass insert. The glass insert was
transferred to a shaker tube, and its contents allowed to thaw
under an ethylene atmosphere. The reaction mixture was agitated
under 6.9 MPa C$_2$H$_4$ for 18 h; during this time the temperature
inside the reactor varied between 25 and 33°C . The final

25 reaction mixture contained polyethylene, which was filtered off,
washed with methanol and dried; yield of polymer = 0.039 g. T$_m$ =
126.2°C as determined by DSC.

(XIV)

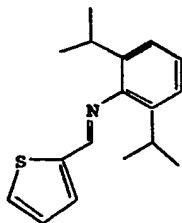30   Example 15

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol)
and anthranilic acid (0.008 g, 0.06 mmol) were dissolved in
benzene (5.0 mL). To the resulting solution was added

HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction

5   mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h; during this time the temperature inside the reactor varied between 25 and 39°C. The final reaction mixture contained polyethylene, which was filtered off, washed with methanol and dried; yield of polymer = 1.74 g. T$_m$ = 118.4°C as determined by DSC.

10   Example 16

Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and compound (XXXVIII) (0.008 g, 0.06 mmol) were dissolved in benzene (5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060 g, 0.06 mmol). The resulting solution was

15   immediately frozen inside a 40 mL shaker tube glass insert. The glass insert was transferred to a shaker tube, and its contents allowed to thaw under an ethylene atmosphere. The reaction mixture was agitated under 6.9 MPa C$_2$H$_4$ for 18 h; during this time the temperature inside the reactor varied between 25 and 34°C.

20   The final reaction mixture contained polyethylene, which was filtered off, washed with methanol and dried; yield of polymer = 1.20 g. T$_m$ = 120.2, 132.3°C as determined by DSC.

(XXXVIII)

25   Example 17

   Synthesis of (VII)

2,6-diisopropylaniline (17.7 g, 100 mmol), 1,2-dibromoethane (9.4 g, 50 mmol), and diisopropylethylamine (20 mL) were heated to reflux for 2 days. Excess diisopropylethylamine was removed from

30   the white crystals in vacuo, and the residue was washed with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ was evaporated to give a red-brown residue. The crude product was recrystallized from methanol to afford white crystals of (VII).

<u>Example 18</u>

<u>Synthesis of (IX)</u>

2,6-Diisopropylaniline (0.89 g, 5.0 mmol) and
pentafluorobenzaldehyde (0.98 g, 5.0 mmol) were dissolved in
5   CH₂Cl₂ (20 mL) and the reaction mixture was stirred overnight at
room temperature. The solvent was removed *in vacuo* to afford 1.5
g of (IX) as an off-white solid.

<u>Example 19</u>

<u>Synthesis of (X)</u>

10   1,1'-Biphenyl-2,2'-diylphosphorochloridite (0.251 g, 1.0
mmol) was dissolved in anhydrous diethyl ether (15 mL) under
nitrogen. To this stirred solution was slowly added the sodium
salt of salicylaldehyde-2,6-diisopropylanilineimine (0.303 g, 1.0
mmol). The solution was stirred for one hour, and then filtered.
15 The filtrate was evaporated to afford a yellow oil. The oil was
redissolved in approximately 3-4 mL petroleum ether. Slow
evaporation of the solution at room temperature gave yellow
crystals of (X). ^{1}H NMR (CDCl₃) d 8.55 (s, 1H, N=CH), 8.25 (d, 1H,
H$_{aryl}$), 7.50-7.05 (mult, 15H, H$_{aryl}$), 2.95 (sept, 2H, C*H*Me₂), 1.15
20 (d, 12H, CH*Me*₂); ^{31}P NMR (CDCl₃) d 142.44.
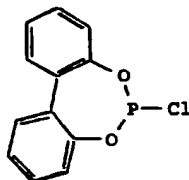
1,1'-biphenyl-2,2'-diylphosphorochloridite
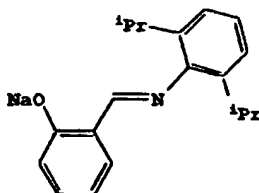
25   salicylaldehyde-2,6-diisopropylanilineimine sodium salt

The preparation of 1,1'-biphenyl-2,2'-
diylphosphorochloridite can be found in the following references:
WO 9303839, U.S. Patents 4,769,498, and 4,688,651, and Cuny, G.D.,
30 et al., *J. Am. Chem. Soc.* vol. 115, p. 2066 (1993).

Salicylaldehyde-2,6-diisopropylanilineimine was prepared by stirring an equimolar mixture of salicylaldehyde and 2,6-diisopropylaniline in the presence of a catalytic amount of formic acid in methanol for several days at room temperature; the product

5   was from pentane at -78°C. The sodium salt was prepared by reaction with sodium hydride in THF.

Example 20

Synthesis of (XI)

Compound (X)I was prepared by the method of Example 19 from

10   6-chloro-6H-dibenz[c,e][1,2]oxaphosphorin and the sodium salt of salicylaldehyde-2,6-diisopropylanilineimine. ^{1}H NMR (CDCl$_3$) d 8.20-7.00 (mult, 16H, N=CH and H$_{aryl}$), 2.80 (sept, 2H, CHMe$_2$), 1.03 (overlapping d's,CHMe$_2$, 12H); ^{31}P NMR (CDCl$_3$) d 128.8ppm.
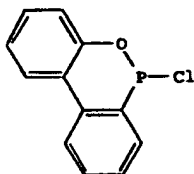
15   6-Chloro-6H-dibenz[c,e][1,2]oxaphosphorin

6-Chloro-6H-dibenz[c,e][1,2]oxaphosphorin was prepared according to a published procedure: Pastor, S.D., et al., *Phosphorus and Sulfur* vol. 31, p. 71 (1987).

Example 21

Synthesis of (XIV)

1,1'-biphenyl-2,2'-diylphosphorochloridite (0.125 g, 0.50

mmol) was dissolved in 15 mL 1:1 anhydrous ether/tetrahydrofuran

5   under nitrogen. To this stirred solution was added the sodium salt

of N-(ortho-hydroxy)benzyl-2,6-diisopropylaniline (0.153 g, 0.50

mmol). Stirring was continued for another 5.5 hours before the

solution was filtered. Evaporation of the filtrate afforded a

nearly colorless oil. This material was redissolved in diethyl

10   ether/petroleum ether (~1:2), and the solution cooled to -40°C. A

small amount of material precipitated from the solution and was

removed. Slow evaporation of the solution afforded white crystals

of compound XIV. ^{1}H NMR (CDCl$_3$) d 7.60-7.00 (mult, 15H, H$_{aryl}$),

4.05 (s, 2H, CH$_2$), 3.40ppm (br s, 1H, NH), 3.25 (sept, 2H, CHMe$_2$);

15   1.10 (d, 12H, CHMe$_2$).
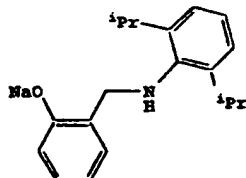
N-(ortho-hydroxy)benzyl-2,6-diisopropylaniline sodium salt

     N-(ortho-hydroxy)benzyl-2,6-diisopropylaniline was prepared

20   by NaBH$_4$ reduction of salicylaldehyde-2,6-diisopropylanilineimine

in CH$_3$OH/CHCl$_3$ (chloroform was added to help solubilize the

aniline starting material). The sodium salt of this compound was

prepared by reaction with sodium hydroxide in tetrahydrofuran.

Example 22

25   Synthesis of (VIII)

     Compound (VIII) was prepared by reduction of N-(ortho-

diisopropylphosphinoxy)benzyl-2,6-diisopropylanilineimine with 2

equivalents of i-Bu$_2$AlH in toluene at 0°C, followed by warming to

room temperature and a basic workup.
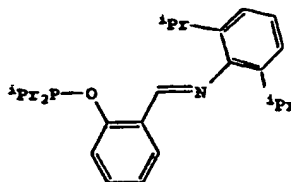
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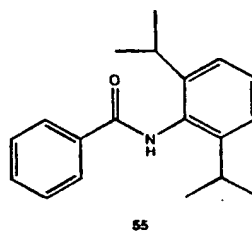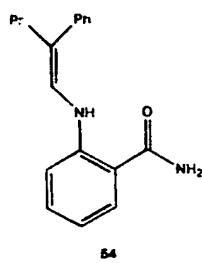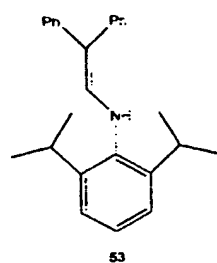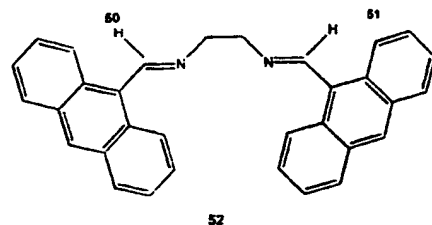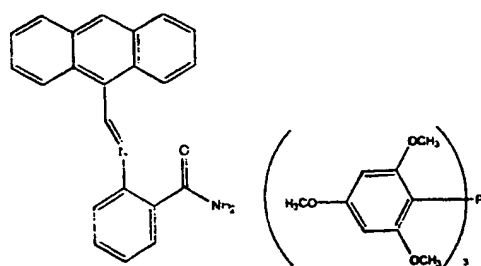N-(ortho-diisopropylphosphinoxy)benzyl-2,6-diisopropylanilineimine

N-(ortho-diisopropylphosphinoxy)benzyl-2,6-
5   diisopropylanilineimine was prepared by reaction of
salicylaldehyde-2,6-diisopropylanilineimine with
chlorodiisopropylphosphine and triethylamine in toluene at room
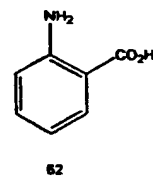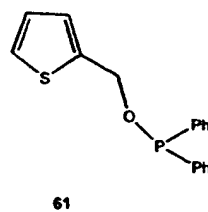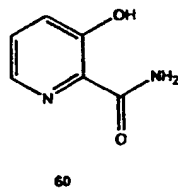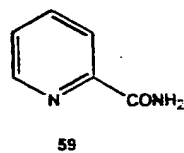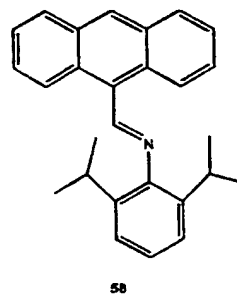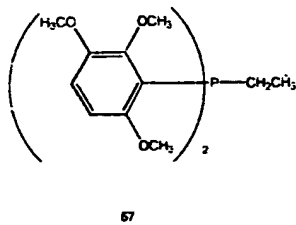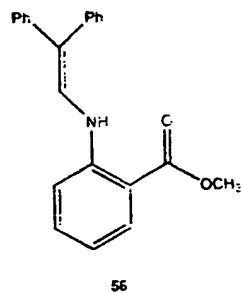temperature.

Examples 23-66

10   These Examples were all done by the same general procedure.
Under a nitrogen atmosphere, Ni(COD)$_2$ (0.017 g, 0.06 mmol) and the
ligand to be tested (0.06 or 0.12 mmol) were dissolved in benzene
(5.0 mL). To the resulting solution was added HBAF·(Et$_2$O)$_2$ (0.060
g, 0.06 mmol). The resulting solution inside a 40 mL shaker tube
15   glass insert was immediately frozen in a freezer inside the glove
box. The glass insert was transferred to a shaker tube, and its
contents allowed to thaw under an ethylene atmosphere of 6.9 MPa.
The reaction mixture was agitated under 6.9 MPa of ethylene
pressure for about 18 h. Any polyethylene in the final reaction
20   mixture was washed with methanol and dried. Melting points of
some of the polymers were determined by DSC. These (when
determined) along with polymer yields and other data are given in
Table 1. The structures of the ligands (except if already shown
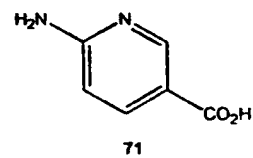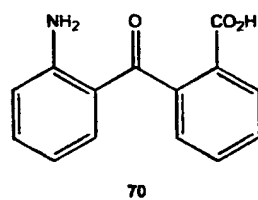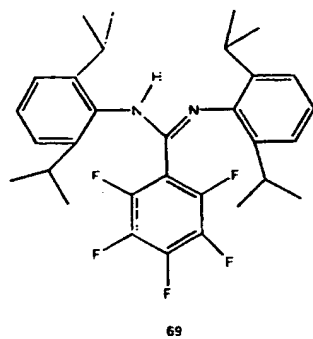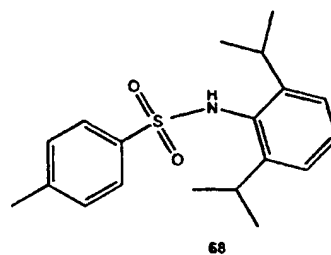above) are listed after Table 1.

<div align="center">Table 1</div>

Ex.	Ligan	Ligand/	q PE	Tm, °C
23	50	1.0	24.4	123
24	51	2.0	15.5	139
25	52	1.0	11.0	-
26	53	2.0	10.2	124
27	54	1.0	5.3	124
28	55	2.0	4.6	125
29	56	1.0	4.3	-
30	57	1.0	4.0	136
31	58	1.0	3.9	118
32	59	1.0	3.6	-
33	60	1.0	3.1	112
34	61	1.0	3.0	124
35	62	1.0	3.0	123
36	63	1.0	2.9	128
37	64	2.0	2.6	-
38	65	1.0	2.1	-
39	66	1.0	1.8	131
40	67	1.0	1.7	118
41	68	1.0	1.6	123
42	69	1.0	1.5	-
43	70	1.0	1.5	-
44	(XIX)	1.0	1.4	121
45	71	1.0	1.3	-
46	(XXV)	1.0	1.3	126
47	72	1.0	1.1	131
48	73	1.0	1.0	-
49	74	1.0	1.0	117
50	75	1.0	.9	-
51	76	1.0	.9	-
52	77	1.0	.9	124
53	78	1.0	.8	-
54	79	2.0	.8	-
55	80	2.0	.7	-
56	81	1.0	.7	127
57	82	1.0	.7	65
58	83	2.0	.6	-
59	(XXII)	1.0	.6	-
60	84	1.0	.6	-
61	85	2.0	.6	-
62	86	2.0	.5	-
63	87	1.0	.5	-
64	88	1.0	.5	-
65	89	2.0	.5	-
66	90	1.0	.4	-

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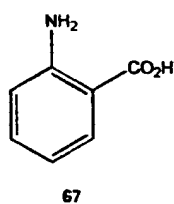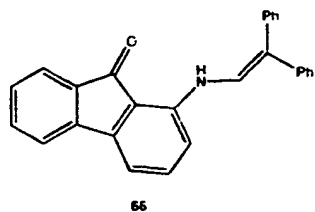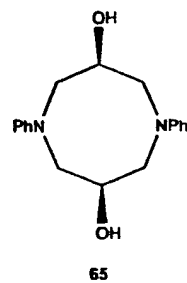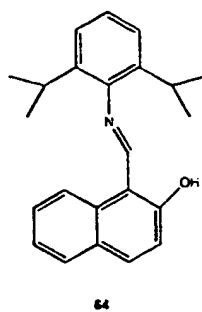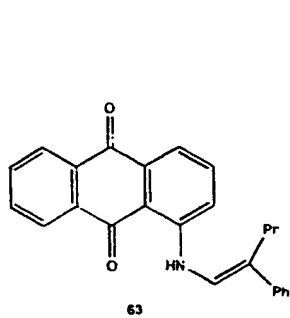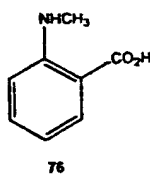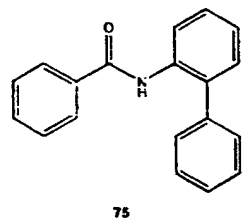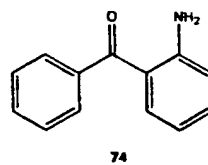
Examples 67-77

Norbornene Polymerization

General procedure: The reactions were carried out in a
dry, deoxygenated atmosphere. The catalyst was weighed into a 20
5 ml glass scintillation vial and a stir bar was added. A solution
of dry dichloromethane/norbornene (3 ml, 43 mass % norbornene) was
added and the resulting solutions stirred for 20-90 h. Each
product was added to stirring methanol (in air) to precipitate the
polymer. The polymer was filtered, washed with methanol/10% HCl
10 solution and methanol and finally dried under vacuum. In each
case purity was improved by redissolving the polymer in chloroform
and reprecipitating with methanol. ^{1}H-NMR (CDCl$_3$) confirmed that
the products were addition polymers of norbornene. Details and
results of these polymerization are given in Table 2. Structures
15 of the catalysts used are shown after Table 2

Table 2

Ex. No.	Catalyst	mmol	Time, h	% Yield	Comments
67	91	0.050	20	>95%	Solution was solidified within 5 min.
68	92	0.041	20	>95%	Solidified over several h
69	93[a]	0.030	20	93%	Exothermic, boiled solvent
70	94	0.016	44	45%	Viscosity increased over several days
71	95[a]	0.036	20	>95%	Exothermic, solidified within 1 min
72	96	0.010	20	94%	Solidified over 1 h
73	98	0.039	20	85%	No stirring after 20 min (too viscous)
74	99	0.019	20	88%	Exothermic, solid within 10 sec
75	100	0.020	20	81%	Exothermic, solid within 5 sec
76	101	0.041	20	>95%	Solidified overnight
77	102	0.018	20	87%	Exothermic, solidified rapidly

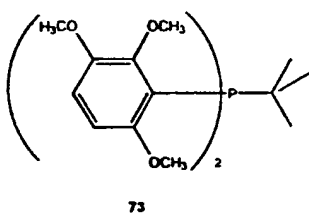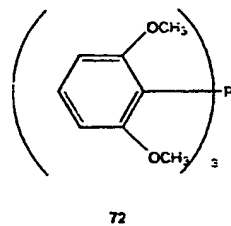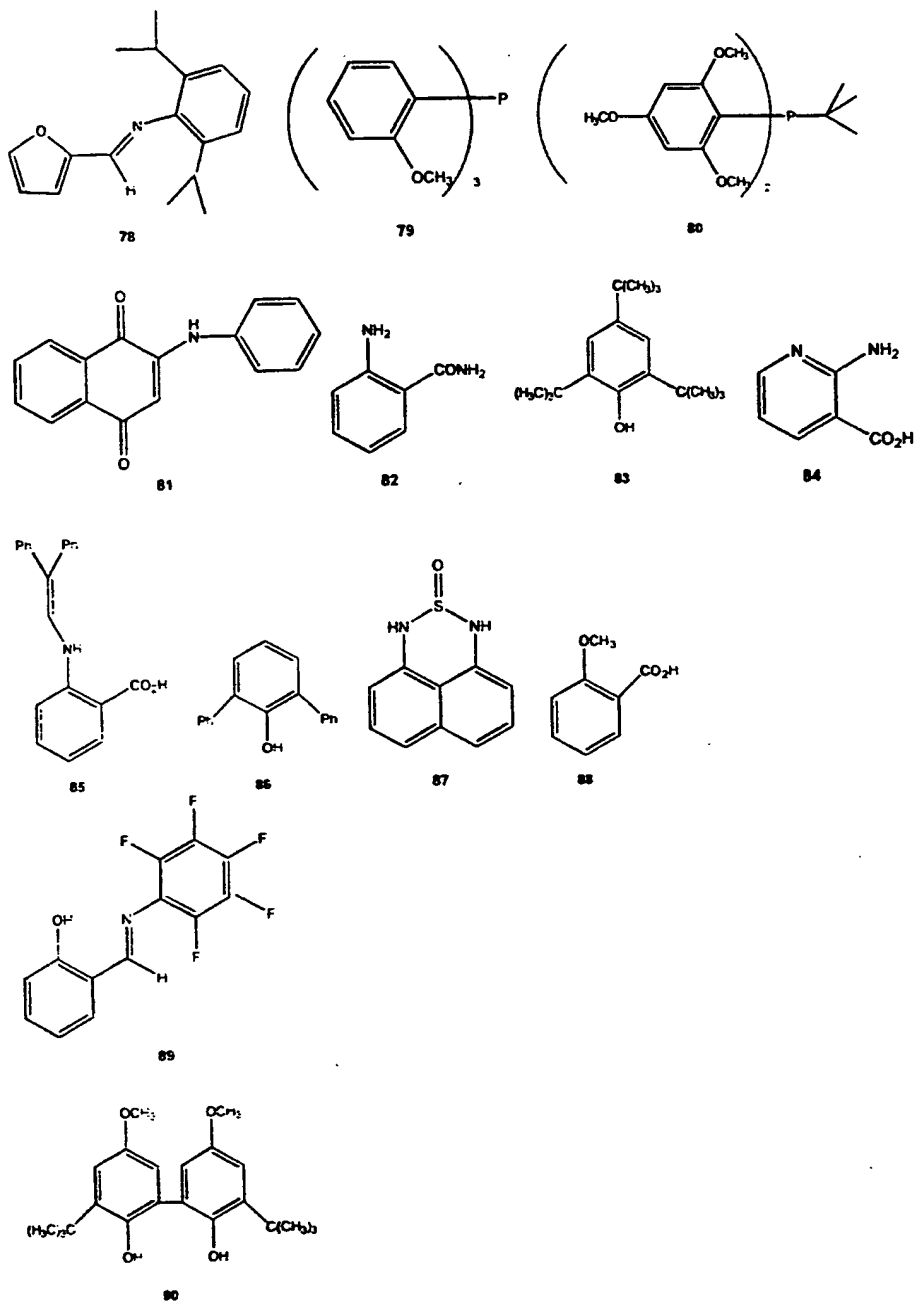[a] End groups visible in ^{1}H NMR of polymer indicate lower molecular weight
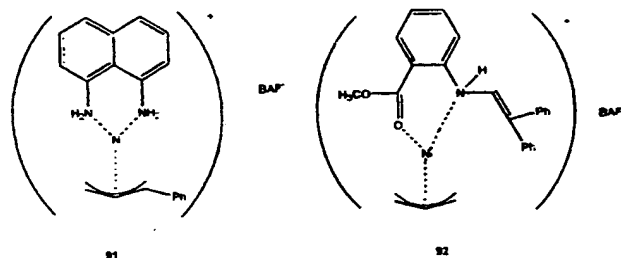
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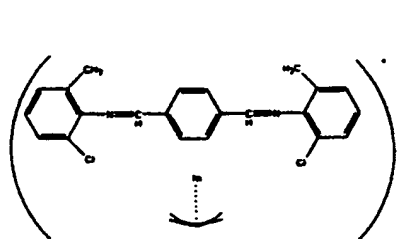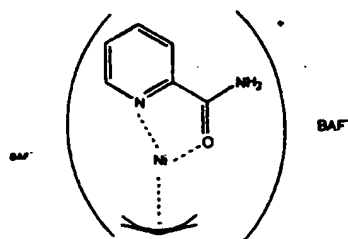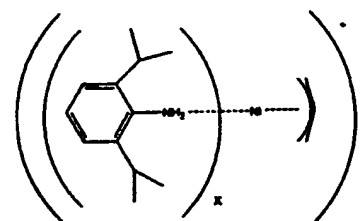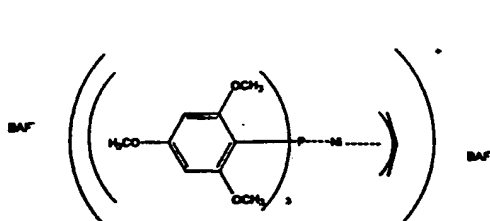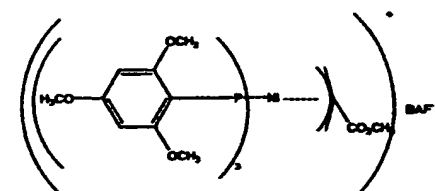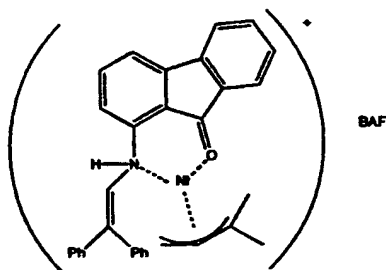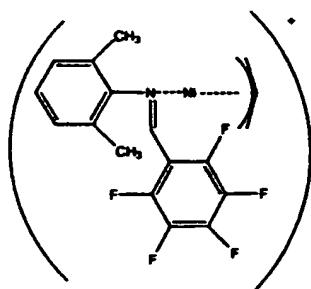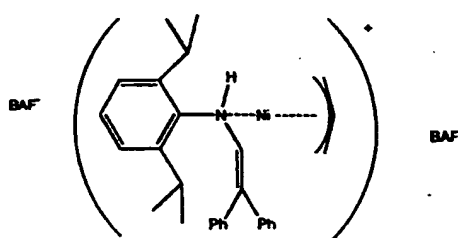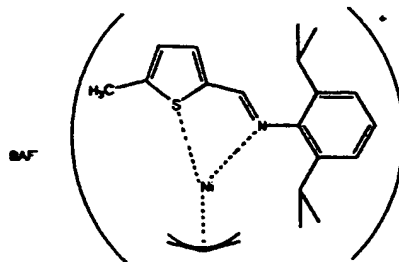
Examples 78-85

Styrene Polymerization

General procedure: The reactions were carried out in a dry, deoxygenated atmosphere. The nickel containing catalyst was weighed into a 20 ml glass scintillation vial and a stir bar added. Dry dichloromethane (2 ml) followed by styrene (2 ml, filtered through alumina, phenothiazine inhibitor) was added and the resulting solutions shaken in the dark for 20 h. The products were added to stirring methanol (in air) to precipitate the polymer. The polymer was filtered, washed with methanol/10% HCl solution and methanol and finally dried under vacuum. Polymers were characterized using ^{13}C-NMR (CDCl$_3$) which indicated that in each case the product was enriched in racemic diad units relative to atactic polystyrene [for measuring tacticities of polystyrenes see T. Kawamura, et al., Macromol. Rapid Commun., vol. 15, p. 479-486 (1994)]. Details of each polymerization and results are shown in Table 3. Structures of catalysts are shown after Table 2, above.

Table 3

| Ex. No.	Catalyst	mmol	% Yield	Comments
78	91	0.017	37%	Golden solution
79	92	0.016	>95%	Brown viscous solution
80	93	0.015	80%	Rapid reaction, viscous brown solution
81	95	0.017	71%	Rapid, orange solution turns brown, viscous
82	96	0.006	6%	Golden solution
83	98	0.016	84%	Boils solvent, dark red viscous solution
84	101	0.016	5%	Yellow solution
85	102	0.027	73%	Yellow solution, rapidly became viscous

Examples 86-94

Styrene/Norbornene Copolymerization

General procedure: The reactions were carried out in a
dry, deoxygenated atmosphere. The catalyst was weighed into a 20

5   ml glass scintillation vial and dry dichloromethane (1 ml) and a
stir bar added. A solution of dry dichloromethane (2 ml), styrene
(2 ml, Aldrich Chemical Co., 99+%, filtered through alumina,
phenothiazine inhibitor added) and 1.5 g norbornene (Aldrich
Chemical Co., 99%) was added and the resulting solutions shaken in
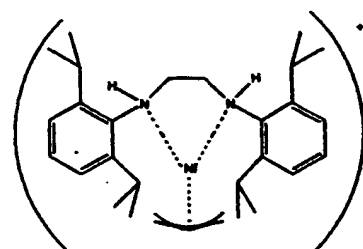
10   the dark for 20 h. The products were added to stirring methanol
(in air) to precipitate the polymer. The polymer was filtered,
washed with methanol/10% HCl solution and methanol and finally
dried under vacuum.

^{1}H-NMR (CDCl$_3$) indicated that in each case the product

15   contained both styrene and norbornene. The absence of a resonance
between 6.2 and 6.7 ppm (assigned to the ortho protons in chains
of polystyrene) confirms that the product is a copolymer [see for
instance A. Benaboura, et al., C.R. Acad. Sc. Paris, Ser. 2, vol.
301, p. 229 (1985)]. The absence of a polystyrene Tg in the DSC

20   confirmed that the products are copolymers.

Details and results of these polymerization are found in
Table 4. Structures of the nickel containing catalysts are shown
after Table 2, above.

Table 4

Ex. No.	Catalyst	mmol catalyst	Polymer Yield (g)	Mol % styrene	Comments
86	91	0.019	0.72g	<5%	Golden solution, sticky polymer
87	92	0.015	1.49g	11.1%	Brown solution, polymer precipitated
88	93	0.012	2.47g	13.7%	Exothermic, precipitated after 5 min
89	95	0.019	2.62g	50.8%	Orange solution turned red, precipitated
90	97	0.013	0.28g	<5%	Brown solution, small amount polymer
91	98	0.019	2.93g	41.4%	Red solution, exothermic, precipitated
92	99	0.009	2.64g	58.1%	Exothermic, golden solution, precipitated
93	100	0.015	2.15g	24.2%	Gold solution, exothermic, precipitated
94	101	0.023	1.54g	5.2%	Yellow solution, polymer precipitated

Examples 95 - 107

Following the procedure of Examples 23 - 66, ethylene was polymerized. The results are reported in Table 5. The structures of the ligands are listed after Table 5.

Table 5

Ex. No.	Ligand	Ligand/Ni	g PE
95	102	1.0	13.8
96	103	1.0	11.6
97	104	1.0	10.8
98	105	1.0	4.3
99	106	1.0	1.8
100	107	1.0	1.5
101	108	1.0	1.4
102	109	1.0	1.2
103	110	1.0	0.9
104	111	1.0	0.6
105	112	1.0	0.4
106	113	1.0	0.4
107	114	1.0	0.2

102

PhS

103

HN

Ph   Ph

104

O   O

NH   NH

105

N

N

106

S   S

107

t-Bu   *t*-Bu

t-Bu

H

N

t-Bu

S

t-Bu

108

N

N

109

Cl   Me

H

N

F

F

F

F

110

N   N

OMe   MeO

111

N

OH

Cl   Cl

112

N

OH

113

O   O

N   N

H   H

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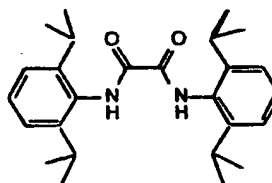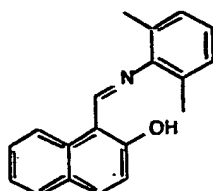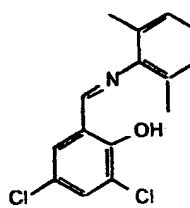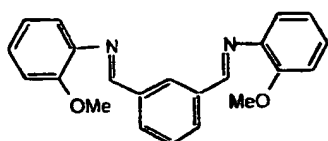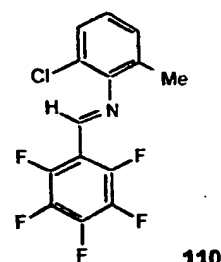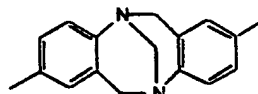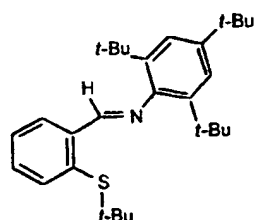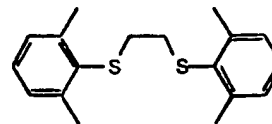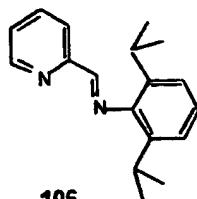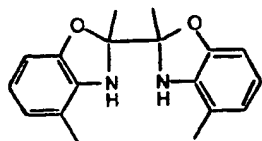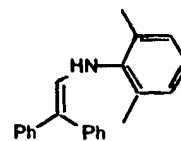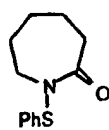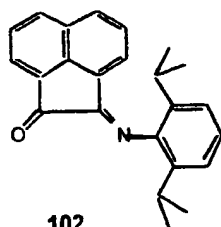
Examples 108-183

General Synthesis of Nickel Allyl Initiators. A mixture of
one to two equiv. of the appropriate ligand, one equiv of NaBAF,
and 0.5 equiv of [(allyl)Ni(m-X)]$_2$ (X = Cl or Br) was dissolved in

5   Et$_2$C. The reaction mixture was stirred for several h before being
filtered. The solvent was removed in vacuo to yield the desired
product. (The [(allyl)Ni(m-X)]$_2$ precursors were synthesized
according to the procedures published in the following reference:
Wilke, G., et al., *Angew. Chem. Int. Ed. Engl.* 1996, 5, 151 -

10   164.) The following ^{1}H and ^{13}C spectroscopic assignments of the
BAF counterion in CD$_2$Cl$_2$ were invariant for different complexes
and temperatures and are not repeated in the spectroscopic data
for each of the cationic allyl complexes: [3,5-C$_6$H$_3$-(CF$_3$)$_2$]$_4^-$
(BAF). ^{1}H NMR (CD$_2$Cl$_2$) d 7.74 (s, 8, H$_o$), 7.57 (s, 4, H$_p$); ^{13}C

15   NMR (CD$_2$Cl$_2$) d 162.2 (q, J$_{CB}$ = 37.4, C$_{ipso}$), 135.2 (C$_o$), 129.3 (q,
J$_{CF}$ = 31.3, C$_m$), 125.0 (q, J$_{CF}$ = 272.5, CF$_3$), 117.9 (C$_p$).

General Procedure for the Screening of Ethylene
Polymerization by Nickel Allyl Initiators. In the drybox, a glass
insert was loaded with the isolated allyl initiator synthesized by

20   the above general procedure. The insert was cooled to -35°C in
the drybox freezer, 5 mL of solvent (typically C$_6$D$_6$ or CDCl$_3$) was
added to the cold insert, and the insert was then capped and
sealed. Outside of the drybox, the cold tube was placed under 6.9
MPa of ethylene and allowed to warm to RT as it was shaken

25   mechanically for approximately 18 h. An aliquot of the solution
was used to acquire a ^{1}H NMR spectrum. The remaining portion was
added to ~ 20 mL of MeOH in order to precipitate the polymer. The
polyethylene was isolated and dried under vacuum.

Example 108

30
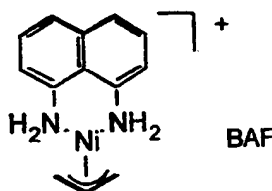
The general synthesis of nickel allyl initiators was
followed using 64 mg of ligand, 53 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and
347 mg of NaBAF. A wheat yellow powder (307 mg) was isolated. ^{1}H
and ^{13}C NMR spectra are consistent with the above structure with

one equiv of Et_2O present. In particular, at -80°C two sets of
amino proton resonances are observed and are coupled to each
other. This is consistent with the above structure in which both
nitrogen atoms are bound to nickel. At room temperature (20°C),
one broad resonance is observed at 5.64 ppm for all of the amino
protons: ^{1}H NMR (CD_2Cl_2, 300 MHz, -80°C) d 7.81 (d, 2, J = 8.09,
H_o or H_p), 7.41 (t, 2, J = 8.1, H_m), 7.26 (d, 2, J = 6.74, H_o or
H_p), 5.49 (m, 1, J = 6.7, H_2CCHCH_2), 5.43 (d, 2, J = 10.8, N$H$$H$'),
5.04 (d, 2, J = 12.14, N$H$$H$'), 3.38 (br q, 4, J = 6.7, O(CH_2CH_3)$_2$),
3.26 (d, 2, J = 6.8 ($H$$H$'CCHC$H$$H$')), 2.17 (d, 2, J = 13.5,
$H$$H$'CCHC$H$$H$'), 0.92 (t, 6, J = 6.1, O(CH_2CH_3)$_2$); ^{13}C NMR (CD_2Cl_2, 75
MHz, rt) d 136.1, 130.4, 129.0, 126.7, 123.2 and 121.7 (C_{aryl}),
115.4 (H_2CCHCH_2), 65.9 (H_2CCHCH_2), 55.7 (O(CH_2CH_3)$_2$), 14.9
(O(CH_2CH_3)$_2$).

Example 109

The allyl initiator of Example 108 was used to polymerize
ethylene in $CDCl_3$ at RT according to the general polymerization
procedure using 24 mg of catalyst. Polyethylene was isolated (304
mg).

Example 110
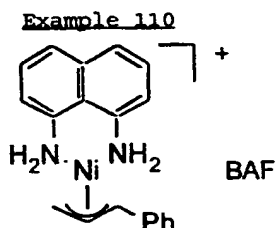
The general synthesis of nickel allyl initiators was
followed using 151 mg of ligand, 205 mg of [($H_2CCHCHPh$)Ni(μ-Cl)]$_2$,
and 860 mg of NaBAF. A yellow-brown powder (694 mg) was isolated.
The ^{1}H NMR spectrum indicates that one equiv of Et_2O is present.
The spectrum, particularly the observation of 4 inequivalent
coupled amino protons, is consistent with the above structure in
which both nitrogen atoms are bound to nickel. The amino
resonances remain inequivalent at least up to 60°C: ^{1}H NMR
(CD_2Cl_2, 300 MHz, -40°C) d 7.85 - 7.25 (m, 10, H_{aryl}), 6.47 (d, 1,
J = 6.8, H_{aryl}), 6.03 (t of d, 1, J = 12.8, 7.2, $H_2CHCHPh$), 5.17
(d, 1, J = 10.8, N$H$$H$'), 4.89 (d, 1, J = 10.8, N$H$$H$'), 4.23 (d, 1, J
= 12.1, N'$H$$H$'), 3.73 (d, 1, J = 12.1, $H_2CHCHPh$), 3.66 (d, 1, J =
10.8, N'$H$$H$'), 3.41 (q, 4, J = 7.2, O(CH_2CH_3)$_2$), 3.34 (d, 1, J =

6.8, *HH*'CHCHPh), 2.31 (d, 1, J = 12.1, H*H*'CCHCHPh), 1.05 (t, 6, J = 7.4, O(CH$_2$C*H*$_3$)$_2$).

Example 111

The allyl initiator of Example 1110 was used to polymerize ethylene in C$_6$D$_6$ at 80°C according to the general polymerization procedure using 67 mg of catalyst. No polyethylene was isolated under these conditions. However, the ^{1}H NMR spectrum of the reaction mixture indicated that butenes and higher olefins were produced in significant amounts.

Example 112
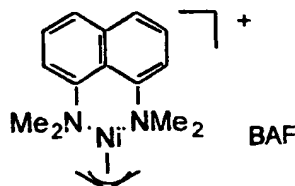
The general synthesis of nickel allyl initiators was followed using 202 mg of ligand, 127 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and 829 mg of NaBAF. A yellow-orange powder (967 mg) was isolated. The NMR spectra are consistent with the structure shown above, in which both nitrogen atoms coordinate to nickel. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) d 7.83 (d of d, 2, J = 5.9, 3.3, H$_m$), 7.56 (s, 2, H$_o$ or H$_p$), 7.54 (d, 2, J = 2.9, H$_o$ or H$_p$), 6.10 (t of t, 1, J = 13.4, 7.1, H$_2$CCHC*H*$_2$), 3.23 (d, 2, J = 7.3, *HH*'CCHC*HH*'), 3.1 (br, 12, 2 x N*Me*$_2$), 2.58 (d, 2, J = 13.2, H*H*'CCHC*HH*'); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt, nonaromatic carbons only) d 117.6 (H$_2$CCHCH$_2$), 60.2 (H$_2$CCHC*H*$_2$), 55.1 (br, N*Me*$_2$).

Example 113

The allyl initiator of Example 112 was used to polymerize
ethylene in $CDCl_3$ at RT according to the general polymerization
procedure (with the exception that 4.1 MPa of ethylene was used)
5   using 40 mg of catalyst. Polyethylene was not isolated. The ^1H
NMR spectrum showed the production of butenes and a small amount
of higher olefins.

Example 114
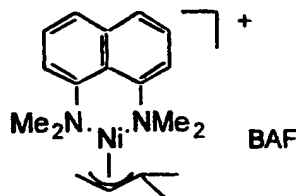
The general synthesis of nickel allyl initiators was
10   followed using 103 mg of ligand, 100 mg of $[(H_2CCHCMe_2)Ni(\mu-Br)]_2$,
and 427 mg of NaBAF. A pale pink powder (517 mg) was isolated.
The NMR spectrum is consistent with the structure shown above, in
which both nitrogen atoms coordinate to nickel. ^1H NMR (CD_2Cl_2,
15   300 MHz, rt) d 8.2 - 7.4 (m, 6, H_{aryl}), 5.33 (dd, 1, J = 12.8,
7.4, $H_2CCHCMe_2$), 3.35 - 2.80 (br, 12, NMeMe', N'MeMe'), 2.78 (dd,
1, J = 8.1, 2.7, HH'CHCMe_2), 1.75 (dd, 1, J = 13.5, 2.7,
HH'CHCMe_2), 1.22 and 0.73 (s, 3 each, $H_2CCHCMeMe'$).

<u>Example 115</u>

The allyl initiator of Example 114 was used to polymerize ethylene in CDCl$_3$ at RT according to the general polymerization procedure using 66 mg of catalyst. Polyethylene was isolated (23

5   mg).

<u>Example 116</u>

The allyl initiator of Example 114 was used to polymerize ethylene in CDCl$_3$ at 80°C according to the general polymerization procedure using 62 mg of catalyst. No polyethylene was isolated;

10   however, the ^{1}H NMR spectrum of the reaction mixture showed the production of butenes, higher olefins, and a broad (CH$_2$)$_n$ peak at 1.25 ppm.

<u>Example 117</u>
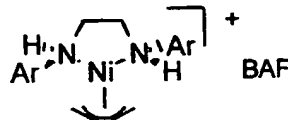
Ar = 2,6-C$_6$H$_3$-i-Pr$_2$

15   The general synthesis of nickel allyl initiators was followed using 135 mg of ligand, 48 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and 307 mg of NaBAF. A yellow powder (394 mg) was isolated. The ^{1}H and ^{13}C NMR spectra are consistent with both nitrogen atoms coordinating to nickel, as shown above, with the aryl rings lying

20   trans to each other in the majority of the product. Other isomers may be present in lesser amounts: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, -40°C) d 7.4 - 7.0 (m, 6, H$_{aryl}$), 5.68 (m, 1, H$_2$CC*H*CH$_2$), 5.53, 5.38, 4.84 and 4.22 (m, 1 each, NC*HH'*C'*HH'*N'), 3.4 - 2.8 (m, 6, N*H*, N'*H*, C*H*Me$_2$, C'*H*Me$_2$, C''*H*Me$_2$, C'''*H*Me$_2$), 2.73 (d, 1, J = 6.7,

25   H*H*'CC*H*C*HH*'), 2.62 (d, 1, J = 6.8, H*H*'CC*H*C*HH*'), 2.39 (d, 1, J = 13.5, H*H*'CC*H*C*HH*'), 1.55 (d, 1, J = 13.5, H*H*'CC*H*C*HH*'), 1.8 - 1.2 (d, 3 each, C*H*Me*Me*', C'*H*Me*Me*', C''*H*Me*Me*', C'''*H*Me*Me*'); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt) d 140.9, 140.8, 139.9, 139.4, 138.9 and 138.4 (Ar: C$_{ipso}$, C$_o$, C$_o$' and Ar': C$_{ipso}$, C$_o$, C$_o$'), 129.0, 128.8, 127.1,

30   127.0, 125.4 and 125.1 (Ar: C$_m$, C$_m$', C$_p$ and Ar': C$_m$, C$_m$', C$_p$), 116.1 (H$_2$CC*H*CH$_2$), 60.7, 55.9, 54.3 and 53.0 (H$_2$CC*H*C'*H*$_2$, NC*H*$_2$C'*H*$_2$N'), 31.7, 30.5, 30.0 and 29.4 (C*H*Me$_2$, C'*H*Me$_2$, C''*H*Me$_2$, C'''*H*Me$_2$), 26.4, 26.0, 24.4, 24.2, 24.2, 24.2, 24.0 and 22.9 (C*H*Me*Me*', C'*H*Me*Me*', C''*H*Me*Me*', C'''*H*Me*Me*').

Example 118

The allyl initiator of Example 117 was used to polymerize ethylene in C_6D_6 at 80°C according to the general polymerization procedure using 63 mg of catalyst. Polyethylene (3.49 g) was

5   isolated. ^1H NMR spectrum of the isolated polymer indicates the formation of branched polyethylene with roughly 100 methyl branches per 1000 carbon atoms.

Example 119

The allyl initiator of Example 117 was used to polymerize

10   ethylene in $CDCl_3$ at 80°C according to the general polymerization procedure using 68 mg of catalyst. Polyethylene (1.69 g) was isolated.
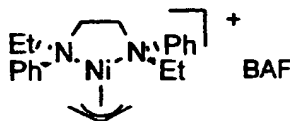
Example 120

15   The general synthesis of nickel allyl initiators was followed using 106 mg of ligand, 53 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and 349 mg of NaBAF. A yellow powder (394 mg) was isolated. The ^1H and ^{13}C NMR spectra are consistent with both nitrogen atoms coordinating to nickel, as shown above, with the aryl rings lying

20   trans to each other in the majority of the product. Other isomers may be present in lesser amounts: ^1H NMR (CD_2Cl_2, 300 MHz, rt) d 8.3 - 7.2 (m, 10, H_{aryl}), 5.9 (m, 1, H_2CCHCH_2), 3.9 - 2.8 (m, 10, $HH'CCHCHH'$, NCH_2CH_2N', NCH_2CH_3, $N'CH_2CH_3$), 2.49 (d, 1, J = 13.6, $HH'CCHCHH'$), 2.15 (d, 1, J = 13.6, $HH'CCHCHH'$), 1.36 and 1.17 (t,

25   3 each, J = 7.2, NCH_2CH_3 and $N'CH_2CH_3$); ^{13}C NMR (CD_2Cl_2, 75 MHz, rt) d 150.1 and 147.5 (Ph: C_{ipso} and Ph': C_{ipso}), 130.8, 130.8, 130.8, 130.7, 129.2, 128.9, 128.2, 124.0, 123.9 and 122.6 (Ph: C_o,C_o', C_m, C_m' and C_p; Ph': C_o, C_o', C_m, C_m' and C_p), 115.6 (H_2CCHCH_2), 59.6, 58.7, 58.3, 57.9, 57.3 and 56.4 (H_2CCHCH_2,

30   NCH_2CH_3, $N'CH_2CH_3$, NCH_2CH_2N'), 12.6 and 11.8 (NCH_2CH_3 and $N'CH_2CH_3$).

Example 121

The allyl initiator of Example 120 was used to polym rize
ethylene in CDCl3 at 60°C according to the general polymerization
procedure using 25 mg of catalyst. A few mg's of soft white
polyethylene was isolated; the ^{1}H NMR spectrum of this product
shows branched polyethylene peaks at 1.25 ppm (CH_2) and 0.85 ppm
(CH_3).

Example 122

The general synthesis of nickel allyl initiators was
followed using 95 mg of ligand, 34 mg of [(C_3H_5)Ni(μ-Cl)]$_2$, and
218 mg of NaBAF. A yellow powder (231 mg) was isolated. The ^{1}H
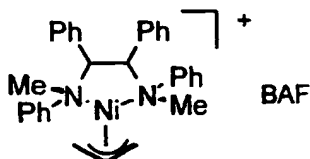NMR spectrum is complex with more than one isomer apparently
present.

Example 123

The allyl initiator of Example 122 was used to polymerize
ethylene in CDCl3 at 60°C according to the general polymerization
procedure using 22 mg of catalyst. A few mg's of polyethylene was
isolated; the ^{1}H NMR spectrum of this product shows a -(CH_2)- peak
at 1.2 ppm. The ^{1}H NMR spectrum of the reaction mixture shows the
production of butenes; branched polyethylene peaks are also
observable at 1.25 ppm (CH_2) and 0.85 ppm (CH_3).

Example 124

Ar = 2,4,6-C_6H_2-(OMe)$_3$
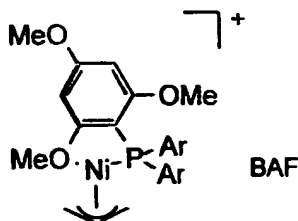
The general synthesis of nickel allyl initiators was
followed using 213 mg of ligand, 54 mg of [(C_3H_5)Ni(μ-Cl)]$_2$, and
354 mg of NaBAF. An orange powder (391 mg) was isolated.
Variable-temperature ^{1}H NMR and ^{13}C NMR spectra are consistent
with the above structure in which one methoxy group and the

phosphorus atom are coordinated to nickel. ^{1}H NMR spectral data
are reported at both -100°C and 20°C. Four resonances for the
allyl syn and anti protons are observed at -100°C, while two
resonances are observed at RT for these protons. The observation

5 of the four syn and anti protons at -100°C supports probable
coordination of the methoxy group to nickel: ^{1}H NMR (CD$_2$Cl$_2$, 300
MHz, -100°C) d 6.05 (d, 6, J_{HP} = 4.1, C$_m$), 5.59 (m, 1, H$_2$CCHCH$_2$),
3.89 (d, 1, J = 6.75, HH'CHC'HH'), 3.76 (s, p-OMe), 3.67 (s, o-
OMe), 3.07 (br s, 1, HH'CHC'HH'), 2.93 (dd, 1, J = 13.5, 5.4,

10 HH'CHCHH'), 1.74 (d, 1, J = 12.1, HH'CCHCHH'); ^{1}H NMR (CD$_2$Cl$_2$, 300
MHz, 20°C) d 6.13 (d, 6, J_{HP} = 2.7, C$_m$), 5.62 (m, 1, H$_2$CCHCH$_2$),
3.81 (s, p-OMe), 3.71 (s, o-OMe), 3.49 (d, 2, J = 6.8, HH'CHCHH'),
2.42 (d, 2, J = 16.2, HH'CHCHH'); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt) d
164.0 (C$_p$), 162.4 (d, J_{CP} = 4.9, C$_o$), 113.7 (H$_2$CCHCH$_2$), 97.8 (d,

15 J_{CP} = 60.4, C$_{ipso}$ to P), 91.1 (d, J = 4.9, C$_m$), 57.8 (H$_2$CCHCH$_2$ and
o-OMe, overlapping), 55.4 (p-OMe).

Example 125

The allyl initiator of Example 124 was used to polymerize
ethylene in CDCl$_3$ at RT according to the general polymerization

20 procedure using 28 mg of catalyst. Butenes were formed according
to ^{1}H NMR spectroscopy.

Example 126

The allyl initiator of Example 124 was used to polymerize
ethylene in C$_6$D$_6$ at RT according to the general polymerization

25 procedure using 28 mg of catalyst. Butenes and some higher
olefins were formed according to ^{1}H NMR spectroscopy.

Example 127

Ar = 2,4,6-C$_6$H$_2$-(OMe)$_3$

The general synthesis of nickel allyl initiators was

30 followed using 501 mg of ligand, 224 mg of [(H$_2$C(CO$_2$Me)CH$_2$)Ni(μ-
Br)]$_2$, and 834 mg of NaBAF. A yellow-green powder (391 mg) was
isolated. ^{1}H NMR spectrum of product is complex; the structure

shown above is tentatively assigned by analogy to the parent
(C$_3$H$_5$) allyl complex.

Example 128

The allyl initiator of Example 127 was used to polymerize
ethylene in C$_6$D$_6$ at RT according to the general polymerization
procedure using 93 mg (0.06 mmol) of catalyst and 2 equiv (29 mg)
of BPh$_3$ cocatalyst. Polyethylene (177 mg) was isolated.

Example 129

The allyl initiator of Example 127 was used to polymerize
ethylene in CDCl$_3$ at RT according to the general polymerization
procedure using 93 mg (0.06 mmol) of catalyst and 2 equiv (61 mg)
of B(C$_6$F$_3$)$_3$ cocatalyst. Polyethylene (90 mg) was isolated.

Example 130
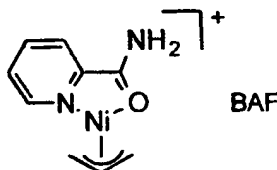
The general synthesis of nickel allyl initiators was
followed using 45 mg of ligand, 50 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and
328 mg of NaBAF. A yellow powder (334 mg) was isolated. The ^{1}H
NMR spectral data is consistent with the structure shown above:
^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) d 8.46 (d, 1, J = 5.4, H$_{aryl}$), 8.17
(t, 1, J = 8.1, H$_{aryl}$), 7.84 (d, 1, J = 8.1, H$_{aryl}$), 7.74 (m, 1,
H$_{aryl}$, overlaps with BAF: H$_o$), 7.10 and 6.82 (br s, 1 each NHH'),
5.99 (m, 1, H$_2$CCHCH$_2$), 3.57 (d, 2, J = 6.8, HH'CCHCHH'), 2.66 (d,
2, J = 13.5, HH'CCHCHH'). ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt) d 173.5
(C=O), 146.4 (C$_{aryl}$: C-C(O)NH$_2$), 153.7, 141.4, 131.6 and 123.9
(C$_{aryl}$ attached to hydrogen), 117.2 (H$_2$CCHCH$_2$), (H$_2$CCHCH$_2$ overlaps
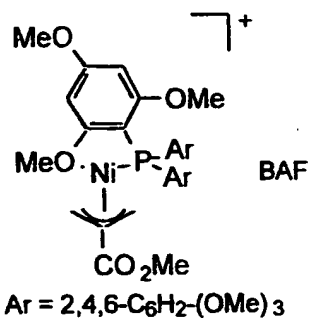with CD$_2$Cl$_2$ resonance).

Example 131

The allyl initiator of Example 130 was used to polymerize
ethylene in CDCl₃ at RT according to the general polymerization
procedure using 63 mg of catalyst. A few mg's of polyethylene was
5 isolated. According to the ^{1}H NMR spectrum of the reaction
mixture, significant amounts of butenes and higher olefins were
produced. Polyethylene -CH₂- resonance is identifiable at 1.25
ppm.

Example 132

10 The allyl initiator of Example 130 was used to polymerize
ethylene in C₆D₆ at 80°C according to the general polymerization
procedure using 64 mg of catalyst. Polyethylene (247 mg) was
isolated. According to the ^{1}H NMR spectrum of the reaction
mixture, the reaction was productive in the formation of butenes
15 and higher olefins.

Example 133

The general synthesis of nickel allyl initiators was
followed using 52 mg of ligand, 50 mg of [(C₃H₅)Ni(μ-Cl)]₂, and
20 328 mg of NaBAF. A yellow powder (328 mg) was isolated. The ^{1}H
NMR spectral data is consistent with the structure shown above:
^{1}H NMR (CD₂Cl₂, 300 MHz, rt) d 11.34 (br s, 1, OH), 8.54 (br s, 1,
NHH'), 7.99 (d, 1, J = 4.0, Haryl), 7.64 (d, 1, J = 8.1, Haryl),
7.55 (t, 1, J = 4.7, Haryl), 6.76 (br s, 1, NHH'), 5.95 (m, 1,
25 HH'CCHCHH'), 3.40 (br, HH'CCHCHH', 2.58 (br, HH'CCHCHH'). ^{13}C NMR
(CD₂Cl₂, 75 MHz, rt, assignments aided by an APT spectrum) δ 173.7
(CO), 155.9 and 133.8 (Caryl not attached to hydrogen), 145.8,
132.3 and 129.3 (Caryl attached to hydrogen), 116.6 (H₂CCHCH₂),
(H₂CCHCH₂ resonances not observed Ñeither overlapping with CD₂Cl₂
30 resonance or broad and in the baseline).

<u>Example 134</u>

The allyl initiator of Example 133 was used to polymerize ethylene in CDCl3 at RT according to the general polymerization procedure using 60 mg of catalyst. Polyethylene (190 mg) was
5   isolated as a white powder.

<u>Example 135</u>

The allyl initiator of Example 133 was used to polymerize ethylene in C_6D_6 at 80°C according to the general polymerization procedure using 60 mg of catalyst. Polyethylene (783 mg) was
10 isolated. According to the ^1H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced.
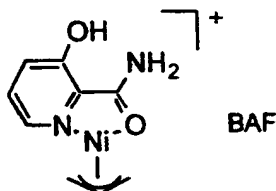
<u>Example 136</u>
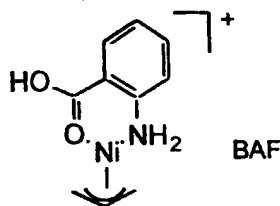
15   The general synthesis of nickel allyl initiators was followed using 57 mg of ligand, 50 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and 328 mg of NaBAF. A yellow powder (264 mg) was isolated. The ^1H, ^{13}C, and APT NMR spectral data is consistent with the structure shown above: ^1H NMR (CD2Cl2, 300 MHz, rt) d 14.0 (br s, 1, O*H*),
20 8.10 (d, 1, J = 8.1, H*aryl*), 7.65 (t, 1, J = 8.1, H*aryl*), 7.47 (t, 1, J = 8.1, H*aryl*), 7.21 (d, 1, J = 8.1, H*aryl*), 5.83 (m, 1, H2CC*H*CH2), 4.34 (br s, 2, N*H2*), 3.23 (br d, 2, J = 5.4, *H*H'CCHC*H*'), 2.34 (br d, 2, J = 13.49, H*H*'CCHCH*H*').

<u>Example 137</u>

The allyl initiator of Example 136 was used to polymerize

ethylene in CDCl₃ at RT according to the general polymerization

procedure using 63 mg of catalyst. Polyethylene was not isolated.

5   According to the ^1H NMR spectrum of the reaction mixture,

significant amounts of butenes and higher olefins were produced.

<u>Example 138</u>

The general synthesis of nickel allyl initiators was

10   followed using 83 mg of ligand, 50 mg of [(C₃H₅)Ni(μ-Cl)]₂, and

328 mg of NaBAF. A red powder (381 mg) was isolated. ^1H NMR

(CD₂Cl₂, 300 MHz, rt): The complex formed a clear red solution in

CD₂Cl₂ with no precipitate present. However, the lock signal and

spectrum were both broad, possibly indicating paramagnetism. The

15   above structure is tentatively assigned by analogy to diamagnetic

complexes containing ligands with similar donor functionality.

Example 139

The allyl initiator of Example 138 was used to polymerize ethylene in CDCl$_3$ at RT according to the general polymerization procedure using 63 mg of catalyst. Polyethylene (88 mg) was

5   isolated.

Example 140

The allyl initiator of Example 138 was used to polymerize ethylene in C$_6$D$_6$ at 80°C according to the general polymerization procedure using 60 mg of catalyst. Polyethylene (64 mg) was

10   isolated. According to the ^{1}H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced.
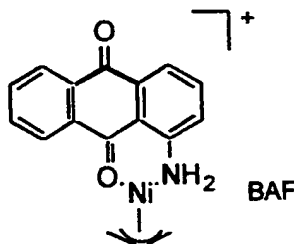
Example 141
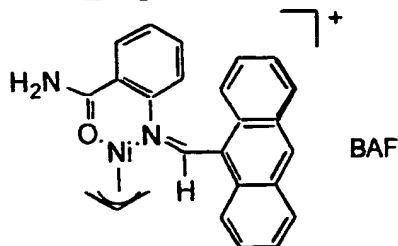
15   The general synthesis of nickel allyl initiators was followed using 135 mg of ligand, 50 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and 328 mg of NaBAF. An orange powder (403 mg) was isolated. The ^{1}H, ^{13}C, and APT NMR spectral data for the major product follows and is consistent with one isomer of the above structure. Other

20   isomers may be present in lesser amounts: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) d 9.77 and 8.83 (s, 1 each, N=CH and H$_{aryl}$), 9.0 - 7.5 (m, 8, H$_{aryl}$), 6.91 and 6.63 (br s, 1 each, NHH'), 4.6 (br s, 1, H$_2$CCHCH$_2$), 3.5 - 2.3 (broad resonances in the baseline, HH'CCHCHH'). ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt, assignments aided by an

25   APT spectrum) d 173.7 (N=CH), 172.9 (CO), 147.4, 131.6, 131.0, 126.5 and 124.7 (C$_{aryl}$ not attached to hydrogen), 136.8, 133.7, 130.3, 130.2, 129.5, 129.3, 127.0, 123.3 and 122.7 (C$_{aryl}$ attached to hydrogen), 113.8 (H$_2$CCHCH$_2$), (H$_2$CCHCH$_2$ resonances were not observedNeither overlapping with CD$_2$Cl$_2$ resonance or broad and in

30   the baseline).

<u>Example 142</u>

The allyl initiator of Example 141 was used to polymerize ethylene in CDCl$_3$ at RT according to the general polymerization procedure using 68 mg of catalyst. Polyethylene (1.60 g) was
5   isolated as a wax.

<u>Example 143</u>

The allyl initiator of Example 141 was used to polymerize ethylene in C$_6$D$_6$ at 80°C according to the general polymerization procedure using 60 mg of catalyst. Polyethylene (5.64 g) was
10   isolated as a wax.

<u>Example 144</u>
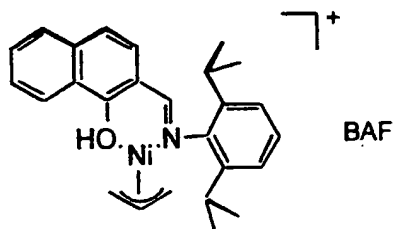
The general synthesis of nickel allyl initiators was followed using 123 mg of ligand, 50 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and
15   328 mg of NaBAF. A yellow powder (383 mg) was isolated. The ^{1}H NMR spectrum is consistent with the above structure, although contamination by free ligand is indicated: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt, i-Pr and allyl resonances only) d 5.97 (m, 1, H$_2$CC*H*CH$_2$), 3.76 (br septet and br d, 1 each, C*H*Me$_2$ and *HH'*CHC*HH'*), 3.53 (br
20   d, 1, J ~ 5.5, H*H'*CCHC*HH'*), 3.35 (br septet, 1, C'*H*Me$_2$), 2.53 (br d, 1, J = 13.6, H*H'*CCHCH*H'*), 2.20 (br d, 1, J = 13.6, HH'CCHC*H*H'), 1.45, 1.43, 1.29 and 1.15 (d, 3 each, J = 6.6 - 7.7, CH*MeMe'* and C'*HMeMe'*).

Example 145

The allyl initiator of Example was 144 used to polymerize ethylene in $CDCl_3$ at RT according to the general polymerization procedure using 40 mg of catalyst. Polyethylene (30 mg) was

5   isolated as a white powder. According to the ^1H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced. Minor resonances consistent with the formation of branched polyethylene are present.

Example 146

10   The allyl initiator of Example 144 was used to polymerize ethylene in C_6D_6 at 80°C according to the general polymerization procedure using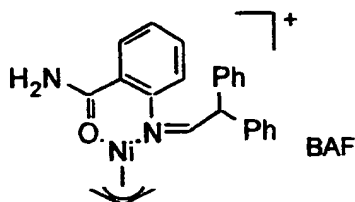 64 mg of catalyst. Polyethylene (96 mg) was isolated as a white powder. The ^1H NMR spectrum shows the production of butenes and higher olefins. Polyethylene $-CH_2-$

15   resonance is identifiable at 1.25 ppm.

Example 147

The general synthesis of nickel allyl initiators was followed using 532 mg of ligand, 229 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and

20   1.50 of NaBAF. 1.85 g of a yellow powder was isolated. Although the free ligand exists as the amine, the ^1H and ^{13}C NMR spectra are consistent with the ligand binding to the molecule as the imine: ^1H NMR (THF-d_8, 300 MHz, rt) d 8.75 (br s, 2, NH_2), 8.55 (d, 1, J = 5.4, N=CH), 7.9 - 7.0 (m, 14, H_{aryl}), 5.56 (d, 1, J =

25   5.4, CHPh$_2$), 5.52 (m, 1, H_2CCHCH_2), 3.01 (d, 2, J = 6.7, HH'CCHCHH'), 2.01 (d, 2, J = 13.5, HH'CCHCHH'); ^{13}C NMR (THF-d_8, 75 MHz, rt, non-aromatic carbons only, assignments aided by APT spectrum) d 181.7 (N=CH), 172.8 (C=O), 113.8 (H$_2$CCHCH2), 58.7 (CHPh$_2$), 54.5 (H$_2$$CCHCH_2$).

Example 148

The allyl initiator of Example 147 was used to polymerize ethylene in CDCl₃ at RT according to the general polymerization procedure using 40 mg of catalyst. Polyethylene (25 mg) was isolated as a white powder. According to the ^{1}H NMR spectrum of the reaction mixture, butenes were formed along with higher olefins; the major product is consistent with branched polyethylene [1.25 (CH_2), 0.85 (CH_3)] with approximately 100 methyl-ended branches per 1000 carbon atoms.

Example 149

The allyl initiator of Example 147 was used to polymerize ethylene in C₆D₆ at RT according to the general polymerization procedure using 75 mg of catalyst. Polyethylene (588 mg) was isolated as a white powder.

Example 150

The allyl initiator of Example 147 was used to polymerize ethylene in C₆D₆ at 80°C according to the general polymerization procedure using 61 mg of catalyst. Polyethylene (1.39 g) was isolated. According to the ^{1}H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced. A significant polyethylene -CH_2- peak appears at 1.25 ppm.

Example 151

The general synthesis of nickel allyl initiators was followed using 255 mg of ligand, 105 mg of [(C₃H₅)Ni(μ-Cl)]₂, and 685 mg of NaBAF. 772 mg of a pale green powder was isolated.

<u>Example 152</u>

The allyl initiator of Example 151 was used to polymerize
ethylene in CDCl₃ at RT according to the general polymerization
procedure using 45 mg of catalyst. Polyethylene (1.61 g) was
5   isolated as a white powder.

<u>Example 153</u>

The allyl initiator of Example 151 was used to polymerize
ethylene in C_6D_6 at RT according to the general polymerization
procedure using 62 mg of catalyst. Polyethylene (93 mg) was
10   isolated as a white powder. The ^1H NMR spectrum shows the
production of butenes and higher olefins. Polyethylene -CH₂-
resonance is identifiable at 1.25 ppm.

<u>Example 154</u>

The allyl initiator of Example 151 was used to polymerize
15   ethylene in C_6D_6 at 80°C according to the general polymerization
procedure using 67 mg of catalyst. Polyethylene (169 mg) was
isolated. According to the ^1H NMR spectrum of the reaction
mixture, the reaction was productive in the formation of butenes
and higher olefins. Polyethylene -CH₂- resonance is identifiable
20   at 1.25 ppm.

<u>Example 155</u>

The general synthesis of nickel allyl initiators was
followed using 213 mg of ligand, 295 mg of [(H₂CC(CO₂Me)CH₂)Ni(μ-
25   Br)]₂, and 795 mg of NaBAF. A gold powder (0.792 g) was isolated.
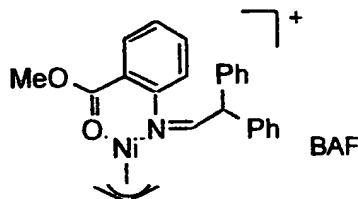
Example 156

The allyl initiator of Example 155 was used to polymerize ethylene in C_6D_6 at RT according to the general polymerization procedure using 61 mg of catalyst. Polyethylene (1.97 g) was
5   isolated as a white powder.

Example 157

The general synthesis of nickel allyl initiators was followed using 657 mg of ligand, 238 mg of $[(H_2CCHCMe_2)Ni(\mu-Br)]_2$,
10 and 1.56 of NaBAF. A red powder (1.88 g) was isolated. Although the free ligand exists as the amine, the ^1H and ^{13}C NMR spectra are consistent with the ligand binding to the molecule as the imine: ^1H NMR (CD_2Cl_2, 300 MHz, rt) d 8.41 (d, 1, J = 5.4, N=CH), 7.8 - 6.8 (m, 17, H_{aryl}), 5.42 (d, 1, J = 5.4, CHPh$_2$), 4.80 (dd,
15 1, J = 12.8, 6.9, H_2CCHCMe$_2$), 2.95 (d, 1, J = 6.7, HH'CCHCMe$_2$), 2.03 (d, 1, J = 13.5, HH'CCHCMe$_2$), 0.77 (s, 6, H_2CCHCMeMe'); ^{13}C NMR (CD_2Cl_2, 75 MHz, rt, non-aromatic carbons only, assignments aided by APT spectrum) d 202.4 (C=O), 182.6 (N=CH), 109.1 (H_2CCHCMe$_2$), 59.7 (CHPh$_2$), 53.2 (H_2CCHCMe$_2$), 43.1 (H_2CCHCMe$_2$),
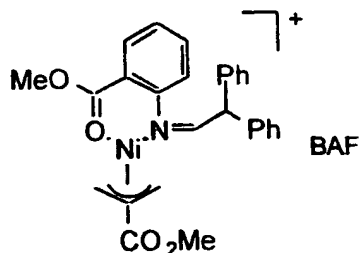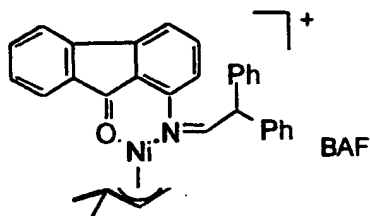20 26.0 and 20.8 (H_2CCHCMeMe').

Example 158

The allyl initiator of Example 157 was used to polymerize ethylene in C_6D_6 at RT according to the general polymerization procedure using 61 mg of catalyst. According to the ^1H NMR
25 spectrum, significant amounts of butenes and higher olefins were produced.

Example 159

The allyl initiator of Example 157 was used to polymerize ethylene in C_6D_6 at 80°C according to the general polymerization
30 procedure using 63 mg of catalyst. According to the ^1H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced

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For Examples 160 - 177 where the ligands are thiophene and furan derivatives, the ^{1}H NMR spectra of the products are, in general, complex and include more than one species. The structural assignments of these complexes are therefore tentative.

Example 160

The general synthesis of nickel allyl initiators was followed using 115 mg of ligand, 50 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and 328 mg of NaBAF. A sticky dark-red solid (185 mg) was isolated.

Example 161

The allyl initiator of Example 160 was used to polymerize ethylene in $CDCl_3$ at RT according to the general polymerization procedure (with the exception that 5.2 MPa of ethylene was used) using 57 mg of catalyst. Polyethylene was not isolated. According to the ^{1}H NMR spectrum of the reaction mixture, significant amounts of butenes and higher olefins were produced.

Example 162

The general synthesis of nickel allyl initiators was followed using 173 mg of ligand, 87 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and 570 mg of NaBAF. An orange powder (705 mg) was isolated.
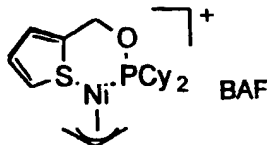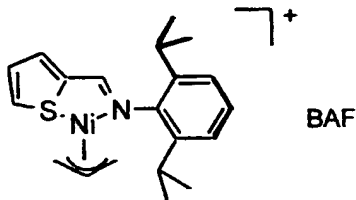
Example 163

The allyl initiator of Example 162 was used to polymerize ethylene in CDCl$_3$ at RT according to the general polymerization procedure using 64 mg of catalyst. Polyethylene (72 mg) was

5   isolated. The ^{1}H NMR spectrum of the reaction mixture indicates that significant amounts of butenes and higher olefins were produced.

Example 164

The allyl initiator of Example 162 was used to polymerize

10   ethylene in C$_6$D$_6$ at 80°C according to the general polymerization procedure using 68 mg of catalyst. Polyethylene (77 mg) was isolated. The ^{1}H NMR spectrum of the reaction mixture indicates that significant amounts of butenes and higher olefins were produced.
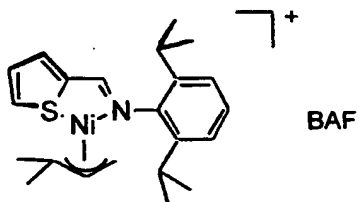
15   Example 165

The general synthesis of nickel allyl initiators was followed using 65 mg of ligand, 50 mg of [(H$_2$CCHCMe$_2$)Ni(μ-Br)]$_2$, and 213 mg of NaBAF. An orange powder (163 mg) was isolated.

<u>Example 166</u>

The allyl initiator of Example 165 was used to polymerize ethylene in $CDCl_3$ at RT according to the general polymerization procedure using 40 mg of catalyst. Polyethylene (823 mg) was

5 isolated as a white powder.

<u>Example 167</u>

The allyl initiator of Example 165 was used to polymerize ethylene in C_6D_6 at 80°C according to the general polymerization procedure using 63 mg of catalyst. Polyethylene was not isolated,

10 however, the ^1H NMR spectrum of the reaction mixture indicates that significant amounts of butenes and higher olefins were formed.

<u>Example 168</u>

15 The general synthesis of nickel allyl initiators was followed using 311 mg of ligand, 274 mg of [($H_2CC(CO_2Me)CH_2$)Ni(μ-Br)]$_2$, and 1.02 g of NaBAF. An orange powder (1.30 g) was isolated.

75

Example 169

The allyl initiator of Example 168 was used to polymerize

ethylene in $CDCl_3$ at 80°C according to the general polymerization

procedure using 77 mg of catalyst and 1 equiv (31 mg) of $B(C_6F_5)_3$

5   cocatalyst. Polyethylene (188 mg) was isolated as a waxy solid.

The ^1H NMR spectrum of the reaction mixture indicates that

significant amounts of butenes and higher olefins were produced;

the polyethylene $-CH_2-$ resonance is identifiable at 1.25 ppm.

Example 170

BAF

10

The general synthesis of nickel allyl initiators was

followed using 323 mg of ligand, 153 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and

1.00 g of NaBAF. An orange powder (1.22 g) was isolated.

Example 171

BAF

15

The general synthesis of nickel allyl initiators was

followed using 329 mg of ligand, 239 mg of $[(H_2CCHCMe_2)Ni(\mu-Br)]_2$,

and 1.02 mg of NaBAF. A sticky red solid (742 mg) was isolated.

Example 172

The allyl initiator of Example 171 was used to polymerize ethylene in C_6D_6 at RT according to the general polymerization procedure using 77 mg of catalyst. Polyethylene (100 mg) was
5   isolated. The ^1H NMR spectrum of the reaction mixture indicates that significant amounts of butenes and higher olefins were produced.
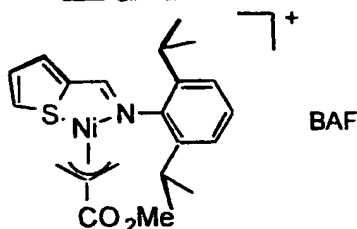
Example 173

10   The general synthesis of nickel allyl initiators was followed using 327 mg of ligand, 272 mg of [(C3H5)Ni(μ-Cl)]2, and 1.01 g of NaBAF. An orange powder (1.42 g) was isolated.
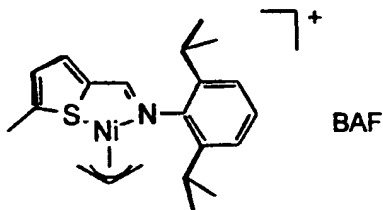
Example 174

The allyl initiator of Example 173 was used to polymerize
15   ethylene in C_6D_6 at RT according to the general polymerization procedure using 78 mg of catalyst and 2 equiv (29 mg) of BPh3 cocatalyst. Polyethylene was not isolated. The ^1H NMR spectrum of the reaction mixture indicates that significant amounts of butenes and higher olefins were produced.
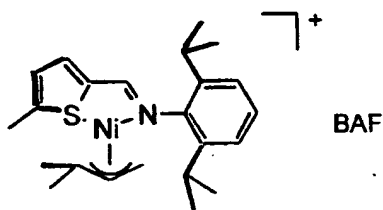
20   ## Example 175

The allyl initiator of Example 173 was used to polymerize ethylene in CDCl3 at 80°C according to the general polymerization procedure using 78 mg of catalyst and 1 equiv (31 mg) of B(C6F5)3 cocatalyst. Polyethylene (2.39 g) was isolated.

25   ## Example 176

The above general procedure for nickel allyl initiators was followed using 62 mg of ligand, 50 mg of [(H2CCHCMe2)Ni(μ-Br)]2, and 213 mg of NaBAF. An orange powder (188 mg) was isolated.

<u>Example 177</u>

The allyl initiator of Example 176 was used to polymerize ethylene in CDCl3 at RT according to the general polymerization procedure using 40 mg of catalyst. No polyethylene was isolated.

<u>Example 178</u>

$$Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$$

The general synthesis of nickel allyl initiators was followed using 462 mg of ligand, 153 mg of $[(C_3H_5)Ni(\mu\text{-}Cl)]_2$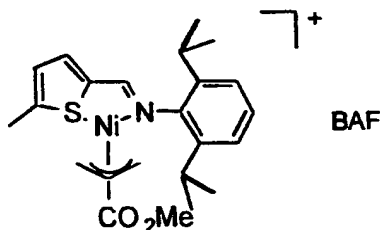, and 1.00 g of NaBAF. A beige powder (1.68 g) was isolated. The stability of the complex is poor in CD_2Cl_2 and THF-d_8 at RT. Only broad NMR spectra were obtained. The above structure is therefore tentatively assigned.

<u>Example 179</u>

The allyl initiator of Example 178 was used to polymerize ethylene in C_6D_6 at RT according to the general polymerization procedure using 82 mg of catalyst. Polyethylene was not isolated.

<u>Example 180</u>

The allyl initiator of Example 178 was used to polymerize ethylene in CDCl3 at 80°C according to the general polymerization procedure using 82 mg of catalyst. Polyethylene (2.01 g) was isolated.

<u>Example 181</u>
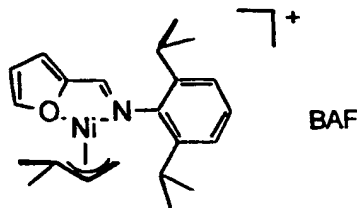
$$Ar = 2,6\text{-}C_6H_3\text{-}Me_2$$

The general synthesis of nickel allyl initiators was followed using 462 mg of ligand, 211 mg of $[(C_3H_5)Ni(\mu\text{-}Cl)]_2$, and 1.36 mg of NaBAF. A pale orange powder (2.16 g) was isolated. The stability of the complex is poor in CD_2Cl_2 and THF-d_8 at RT. Only broad NMR spectra were obtained. The above structure is therefore tentatively assigned.
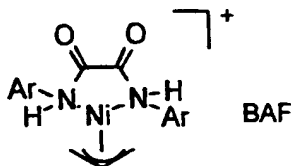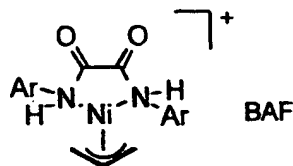
<u>Example 182</u>

The allyl initiator of Example 181 was used to polymerize
ethylene in C_6D_6 at RT according to the general polymerization
procedure using 76 mg of catalyst. Polyethylene (147 mg) was
isolated.

<u>Example 183</u>

The allyl initiator of Example 181 was used to polymerize
ethylene in $CDCl_3$ at 80°C according to the general polymerization
procedure using 76 mg of catalyst. Polyethylene (434 mg) was
isolated.

<u>Examples 184 - 177</u>

Following the procedure of Examples 23 - 66, ethylene was
polymerized. The results are reported in Table 6. The structures
of the ligands are listed after Table 6.

Table 6

Ex. No.	Ligand	Ligand/Ni	g. PE	Tm, °C
184	115	1	9.0	125
185	116	1	2.4	-
186	117	2	2.7	-
187	118	1	5.0	-

115   116   117

20

11s
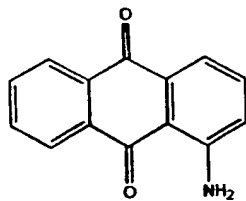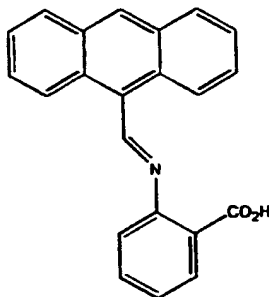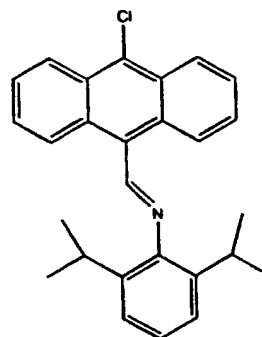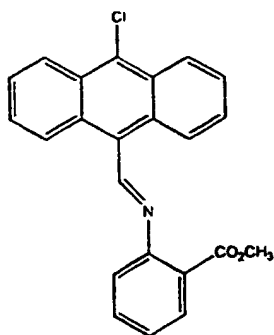
Example 188

Synthesis of 50

9-Anthraldehyde (3.70 g) was dissolved in 100 ml THF in a
200 ml round bottom flask. To the hot solution was added dropwise
2.77g 2-anthranilamide (in 20 ml THF). Then 4 drops of formic
acid were added to the mixture. Soon after adding the formic
acid, yellow precipitate began to form. Heating and stirring were
continued for another 2 h. After cooling, the solid was isolated
by filtering, followed by washing with methanol and THF to remove
excess 2-anthranilamide. TLC (5:1 hexane:ethyl acetate) showed a
single new band. The dried product weighed 3.5g. ^{1}H NMR (DMSO, δ
in ppm):9.82(s, 1H);8.90(m, 3H);8.25(m, 3H);7.90(d, 1);7.67.7(m,
7H);7.45(t, 1).

Example 189

Synthesis of 66

1,1-Diphenylacetaldehyde (0.4906 g) was dissolved in 30 ml
methanol. To this hot solution was added 0.4881 g
1-amino-9-fluorenone (in methanol). Then 6 drops of formic acid
was added to catalyze the reaction. Soon after adding the formic
acid, the color of the solution changed from yellow to orange red,
then to deep red. At this point, TLC (3:1 hexane:ethyl acetate)
showed the appearance of new bands. When cooled, a red
precipitate formed. The precipitate was isolated by filtering
followed by washing with methanol and hexane. The dried product
weighed 0.4g. The ^{1}H, ^{13}C and APT spectra are consistent with the
existence of the product as the enamine structure shown above. In
addition the structure was confirmed by X-ray crystallography. ^{1}H
NMR (CD$_2$Cl$_2$, 300 MHz, rt) d 9.25 (d, 1, J = 12.1, NH), 7.6 - 6.85
(m, 18, H$_{aryl}$ and CH=CPh$_2$); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt,

assignments were aided by an APT spectrum) d 194.0 (C=O), 144.6,

143.1, 142.7, 141.2, 137.7, 134.7 121.3 and 115.15 (C_{aryl} not

attached to hydrogen and =CPh_2), 136.6, 133.6, 130.1, 129.2,

128.9, 128.3, 127.6, 126.5, 126.1, 123.1, 121.9, 120.4, 112.7 and

5   110.8 (C_{aryl} attached to hydrogen and =CHNHAr).

Example 190

Synthesis of 63

1-Aminoanthraquinone (2.2323 g) was dissolved in a 1:1

mixture of methanol and THF. To the hot solution was added

10   1.9625g 1,1-diphenylacetaldehyde. Then 8 drops of formic acid was

added as catalyst. After refluxing for 4 h, heating was removed.

TLC (5:1 hexane:ethyl acetate) showed the appearance of a new band

which was purple. The solvent was removed by rotary evaporator.

The solid was resuspended in ether and stirred. Filtered to

15   collect the solid, followed by washing with a large amount of

ether until a single band was obtained. Pure product was also

obtained by silica gel chromatography to give a purple solid.

Yield 1.2g. ^{1}H NMR (CD_2Cl_2, δ in ppm):11.75(d, 1H);8.20(m,

2H);7.25-7.85(m, 16H).

20   ## Example 191

Synthesis of 54

1,1-Diphenylacetaldehyde (3.9250 g) was dissolved in 30 ml

anhydrous methanol. To this refluxing solution was added 2.7230 g

2-anthranilamide (in methanol). Soon a yellow precipitate formed.

25   After all the 2-anthranilamide was added, heating and stirring

were continued for another hour. When cooled, the solid was

isolated by filtering. The solid was then resuspended in

methanol, stirred and then filtered. Yield 5.1g. The ^{1}H, ^{13}C,

and APT spectra are consistent with the existence of the product

30   as the enamine structure shown above: ^{1}H NMR (THF-d_8, 300 MHz,

rt, assignments were aided by an APT spectrum) δ 10.86 (br d, 1, J

= 12.10, NH-CH=CPh_2), 7.60 - 6.85 (m, 16, H_{aryl}, CH=CPh_2,

C(O)NHH'), 6.60 (br s, 1, C(O)NHH'); ^{13}C NMR (THF-d_8, 75 MHz, rt,

assignments were aided by an APT spectrum) δ 171.9 (C=O), 145.9,

35   143.4, 139.7, 120.0 and 116.6 (C_{aryl} not attached to hydrogen and

=CPh_2), 113.4, 131.1, 129.4, 128.8, 127.4, 125.9, 124.9, 117.8 and

113.4 (C_{aryl} attached to hydrogen and =CHNAr).

<u>Example 192</u>

<u>Synthesis of 56</u>

1,1-Diphenylacetaldehyde (4.0138 g) was dissolved in 20 ml
anhydrous methanol. To this hot solution was added 3.0918 g
5   methyl anthranilate (in methanol). The color of the solution
changed from colorless to yellow as soon as two components were
mixed. After adding all the methyl anthranilate, the heat was
turned off. During cooling, a yellow precipitate began to form.
The precipitate was collected by filtering followed by washing
10 with methanol. After recrystallization in methanol, 2.6g product
was obtained.

The ^{1}H, ^{13}C, and APT spectra are consistent with the
existence of the product as the enamine structure shown above. In
addition, this structure was confirmed by X-ray crystallography.
15 ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) δ 9.94 (br d, 1, J = 11.73, NH), 8.05
- 6.75 (m, 15, H$_{aryl}$ and =CHNHAr), 3.78 (s, 3, OMe); ^{13}C NMR
(CD$_2$Cl$_2$, 75 MHz, rt, assignments were aided by an APT spectrum) δ
168.0 (C=O), 145.4, 141.9, 138.4, 120.9 and 112.1 (C$_{aryl}$ not
attached to hydrogen and CH=CPh$_2$), 134.6, 132.0, 130.3, 129.0,
20 128.4, 127.3, 126.7, 125.9, 123.4, 117.7 and 112.4 (C$_{aryl}$ attached
to hydrogen and CH=CPh$_2$), 51.8 (OMe).
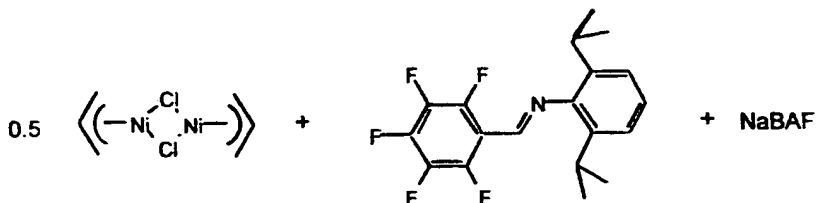
Example 193

Synthesis of 58

9-Anthraldehyde (2.0624 g) was dissolved in 60 ml of a 1:1 mixture of methanol and THF (the 9-anthralaldehyde did not

5   dissolve completely in methanol). To this refluxing solution was added dropwise 1.7729g 2,6-diisopropylaniline. When the addition was complete, 4 drops of formic acid were added as catalyst. The solution was refluxed for another 2 h before it was cooled. After standing overnight, a yellow solid precipitated. The solid was

10 isolated by filtering followed by washing with methanol. Yield 2.5g of dried product. ^{1}H NMR (CD$_2$Cl$_2$, δ in ppm): 9.51(s, 1H);9.05(d, 2H);9.20(s, 1H);8.20(d, 2H);7.65(m, 4H);7.30(d, 2H);7.25(t, 1H);3.30(hep, 2H);1.30(d, 12H).

Example 194

15
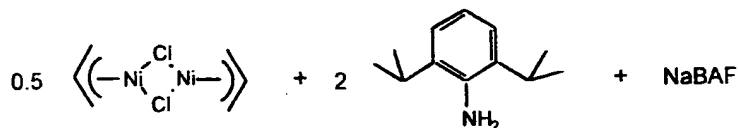
The general synthesis of nickel allyl initiators was followed using 136 mg of ligand, 53 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and 342 mg of NaBAF. A yellow powder (430 mg) was isolated.

Example 195.

20 The allyl initiator of Example 194 was used to polymerize ethylene in C$_6$D$_6$ at 80°C according to the general polymerization procedure using 64 mg of catalyst. Polyethylene (104 mg) was isolated. The ^{1}H NMR spectrum of the reaction mixture showed that significant amounts of butenes and higher olefins were produced.

25 Example 196

The general synthesis of nickel allyl initiators was followed using 129 mg of ligand, 51 mg of [(C$_3$H$_5$)Ni(μ-Cl)]$_2$, and 317 mg of NaBAF. A sticky orange solid (217 mg) was isolated.

<u>Example 197</u>

The allyl initiator of Example 196 was used to polymerize
ethylene in $CDCl_3$ at 60°C according to the general polymerization
procedure using 24 mg of catalyst. The ethylene pressure was
5　initially 1.2 MPa and was increased to 6.9 MPa after 1 h. A few
mg's of polyethylene was produced. The ^1H NMR spectrum of the
reaction mixture showed that significant amounts of butenes and
higher olefins were produced.

<u>Example 198</u>

10

The general synthesis of nickel allyl initiators was
followed using 136 mg of ligand, 49 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and
309 mg of NaBAF. An orange powder (380 mg) was isolated.

<u>Example 199</u>

15　The allyl initiator of Example 198 was used to polymerize
ethylene in C_6D_6 at RT at 5.2 MPa according to the general
polymerization procedure using 63 mg of catalyst. Polyethylene
(29 mg) was isolated. The ^1H NMR spectrum of the reaction mixture
showed that significant amounts of butenes and higher olefins were
20　produced.
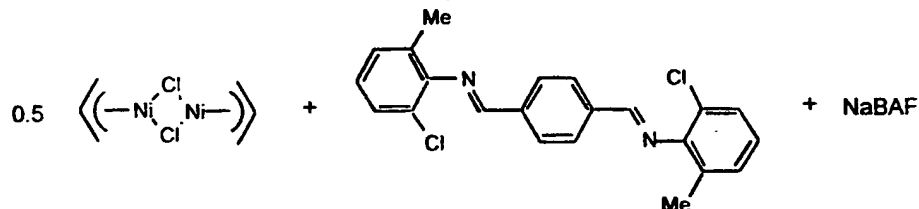
<u>Example 200</u>

The general synthesis of nickel allyl initiators was
followed using 111 mg of ligand, 50 mg of $[(C_3H_5)Ni(\mu-Cl)]_2$, and
25　328 mg of NaBAF. An orange powder (347 mg) was isolated.
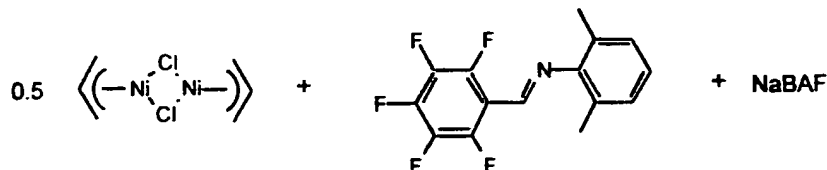
Example 202

The allyl initiator of Example 201 was used to polymerize
ethylene in CDCl$_3$ at 60°C according to the general polymerization
procedure using 23 mg of catalyst. The ethylene pressure was

5   initially 1.4 MPa and was increased to 6.9 MPa after 1 h. A few
mg's of polyethylene was produced. The ^{1}H NMR spectrum of the
reaction mixture showed that significant amounts of butenes and
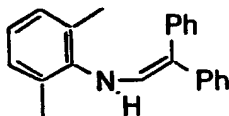higher olefins were produced.

Example 203

10

Using 5.47 g of 1,1-diphenylacetaldehyde and 3.60 g of 2,6-
dimethylaniline, 5.79 g of an orange powder was obtained following
a synthesis analogous to that of the 2,6-diisopropylaniline
derivative given above. The ^{1}H, ^{13}C, and APT spectra are

15   consistent with the existence of the product as the enamine
structure shown above: ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 7.6 - 7.0
(m, 13, H$_{aryl}$), 6.88 (d, 1, J = 12.1, ArNHCH=CPh$_2$), 5.47 (d, 1, J
= 12.1, ArNHCH=CPh$_2$), 2.37 (s, 6, C$_6$H$_3$-Me_2); ^{13}C NMR (CDCl$_3$, 75
MHz, rt, assignments aided by an APT spectrum) δ 142.0, 140.7,

20   138.9 and 131.1 (Ph: C$_{ipso}$; Ph': C$_{ipso}$; Ar: C$_{ipso}$ and C$_o$), 131.6,
130.6, 129.3, 128.9, 128.3, 126.9, 125.4, 124.8 and 123.8 (Ph: C$_o$,
C$_m$, C$_p$; Ph': C$_o$, C$_m$, C$_p$; Ar: C$_m$, C$_p$; CH=CPh$_2$), 114.0 (CH=CPh$_2$),
13.8 (C$_6$H$_3$-Me_2).

Example 204

25
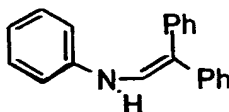
Using 5.43 g of 1,1-diphenylacetaldehyde and 2.71 g of
aniline, 5.68 g of yellow powder was obtained following a
synthesis analogous to that of the 2,6-diisopropylaniline
derivative given above. The ^{1}H, ^{13}C, and APT spectra are

30   consistent with the existence of the product as the enamine
structure shown above: ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 7.6 - 6.8
(m, 15, H$_{aryl}$), 7.18 (d, 1, J = 12.1, PhNHCH=CPh$_2$), 6.12 (d, 1, J
= 11.8, PhNHCH=CPh$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz, rt, assignments were
aided by an APT spectrum) δ 142.7, 141.8 and 138.5 (Ph: C$_{ipso}$;

Ph': C$_{ipso}$; Ph'': C$_{ipso}$), 130.5, 129.6, 129.3, 128.4, 127.2, 126.2, 125.5, 124.8, 120.0 and 113.9 (Ph: C$_o$, C$_m$, C$_p$; Ph': C$_o$, C$_m$, C$_p$; Ph'': C$_o$, C$_m$, C$_p$; CH=CPh$_2$), 117.7 (CH=CPh$_2$).

<u>Example 205</u>
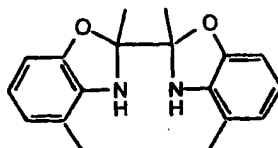
5

    solution of 1.02 g of 2,3-butanedione in 10 mL of MeOH and 2.92 g of 2-amino-m-cresol were mixed together in a round bottom flask. Formic acid (10 drops) was added via pipette. After ~1.5 h, a precipitate had formed. The solution was stirred overnight

10 and the next day the precipitate was collected on a frit and washed with methanol. The product was then dissolved in Et$_2$O and stirred overnight over Na$_2$SO$_4$. The solution was filtered through a frit with Celite and the solvent was removed in vacuo. A light pink powder was obtained (1.72 g). The ^{1}H and ^{13}C are consistent

15 with the product existing as the cyclized diamine rather than as the diimine. [Note: Literature precedent for this cyclization reaction exists, such as in the reaction of o-aminophenol with glyoxal or the reaction of o-aminobenzoic acid with glyoxal. See: Kliegman, J. M.; Barnes, R. K. *J. Org. Chem.* 1970, 35, 3140 –

20 3143.]: ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 6.9 – 6.5 (m, 6, H$_{aryl}$), 4.58 (s, 2, NH), 2.20 and 1.62 (s, 6 each, Me, Me'); ^{13}C NMR (CDCl$_3$, 75 MHz, rt) δ 141.7, 127.1 and 122.3 (Ar: C$_{ipso}$, C$_o$, C$_o$'), 122.6, 119.8, 114.9 (Ar: C$_m$, C$_m$', C$_p$), 82.0 (-OC(Me)NH-), 22.1 and 16.7 (Me, Me').

25   <u>Example 206</u>
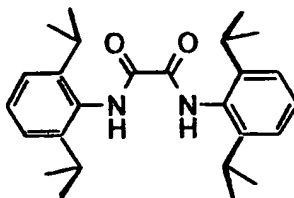
    n a nitrogen-filled drybox, 20.01 g of lithium 2,6-diisopropylanilide was placed in a 2-neck round bottom flask and dissolved in 300 mL of Et$_2$O. A 60 mL solution of 6.93 g of oxalyl

30 chloride was placed in an addition funnel. The oxalyl chloride was added to the reaction mixture over a period of several hours

and the mixture was then stirred overnight. Some of the product
precipitate out of the Et$_2$O solution along with the LiCl. Some of
the Et$_2$O was removed in vacuo and enough THF was added to dissolve
the product. The solution was filtered through a frit with

5   Celite, the Celite was washed with THF, and the solvent was
removed in vacuo. The product was washed with pentane and pumped
dry to give 20.72 g of an off-white powder: ^{1}H NMR (CDCl$_3$, 300
MHz, rt) δ 9.26 (br s, 2, NH), 7.23 - 7.04 (m, 6, H$_{aryl}$), 2.94
(septet, 4, CHMe$_2$), 1.09 (d, 24, CHMe$_2$).

10
Example 207
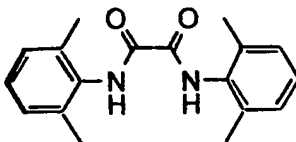
Following the synthetic procedure of the above example, 7.49
g of oxalyl chloride and 15.00 g of lithium 2,6-dimethylanilide
was used to synthesize 23.98 g of product, which was isolated as

15 an off-white powder: ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 9.53 (br 2, 2,
NH), 7.00 - 6.86 (m, 6, H$_{aryl}$), 2.10 (s, 12, Me).

Example 208
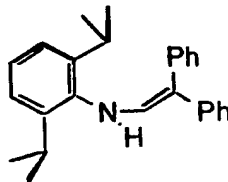
Formic acid catalyst (~ 1 mL) was added to a methanol

20 solution of diphenylacetaldehyde (4.44 mL) and 2,6-
diisopropylaniline (3.18 mL). After ~ 15 minutes of stirring, a
white precipitate formed. The reaction mixture was stirred for
several days before the precipitate was collected on a frit and
washed with methanol. The product was then dissolved in Et$_2$O and

25 stirred over Na$_2$SO$_4$ overnight. The solution was filtered through
a frit with Celite and the solvent was removed in vacuo to yield
the product. The ^{1}H, ^{13}C, and APT spectra are consistent with the
existence of the product as the enamine structure shown above: ^{1}H
NMR (CD$_2$Cl$_2$, 300 MHz, rt) δ 7.6 - 7.0 (m, 13, H$_{aryl}$), 6.71 (d, 1,

30 J = 12.1, =CHNHAr), 5.37 (d, 1, J = 12.5, NHAr), 3.34 (septet, 2,
J = 6.9, CHMe$_2$), 1.25 (d, 12, J = 7.0, CHMe$_2$); ^{13}C NMR (CD$_2$Cl$_2$,
300 MHz, rt, assignments were aided by an APT spectrum) δ 144.9

(Ar: C_o), 142.5, 139.3 and 138.5 (Ar: C_{ipso}, Ph: C_{ipso}, Ph':
C_{ipso}), 133.9, 130.9, 129.7, 128.6, 127.2, 126.2, 125.4, 124.7 and
124.0 (Ph: C_o, C_m, C_p; Ph': C_o, C_m, C_p; Ar: C_m, C_p, $Ph_2C=CH$),
113.4 ($Ph_2C=CH$), 28.6 ($CHMe_2$), 23.9 ($CHMe_2$).
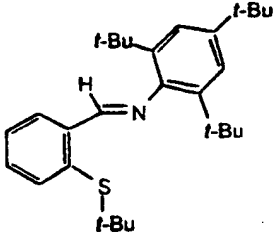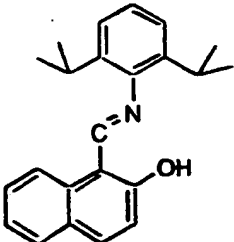
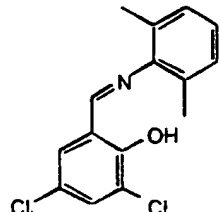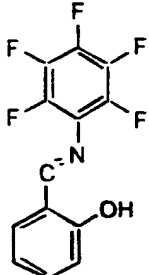5   Examples 209-217
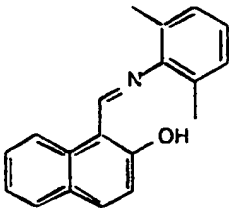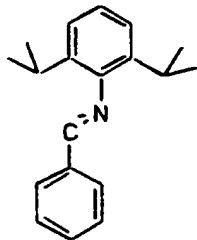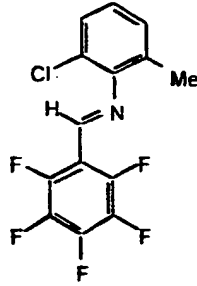
The imines in the following table were synthesized using
Procedures A and B below. Details are shown in the Table.
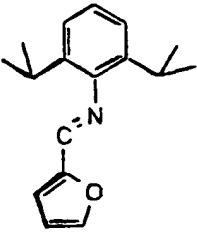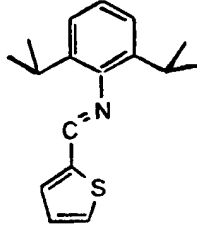
A. Formic acid catalyst was added to a methanol solution of
the aldehyde and the aniline. The reaction mixture was stirred
10   and the resulting precipitate was collected on a frit and washed
with methanol. The product was then dissolved in Et_2O or CH_2Cl_2
and stirred over Na_2SO_4 overnight. The solution was filtered
through a frit with Celite and the solvent was removed in vacuo to
yield the product.

15   B. A CH_2Cl_2 solution of the aldehyde and the aniline was
stirred over sodium sulfate. The solution was filtered through a
frit with Celite and the solvent was removed in vacuo. If
necessary, the product was purified by heating in vacuo to remove
excess aniline and/or by recrystallization.

20

Example	Ligand	Synthesis and NMR Data
209		Procedure A. ^1H NMR ($CDCl_3$, 300 MHz, rt) δ 8.97 (s, 1, CH=N), 8.43 (dd, 1, J = 7.8, 1.6, H_{aryl}), 7.64 (dd, 1, J = 7.6, 1.3, H_{aryl}), 7.55 (t, 1, J = 7.2, H_{aryl}), 7.46 (td, 1, J = 7.4, 1.7, H_{aryl}), 7.37 (s, 2, H_{aryl}), 1.37 (s, 9, CMe_3), 1.28 (s, 18, CMe_3), 1.21 (s, 9, CMe_3).
210		Procedure A. ^1H NMR ($CDCl_3$, 300 MHz, rt) δ 15.30 (s, 1, OH), 9.09 (s, 1, N=CH), 8.1 - 7.2 (m, 9, H_{aryl}), 3.12 (septet, 2, $CHMe_2$), 1.25 (d, 12, $CHMe_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 161.7 (C=N).

211		Procedure A. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 15.3 (s, 1, OH), 9.23 (s, 1, N=CH), 8.4 - 7.1 (m, 9, H$_{aryl}$), 2.41 (s, 6, Me).
212		Procedure A. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 14.15 (s, 1, OH), 8.43 (s, 1, N=CH), 7.7 - 7.1 (m, 5, H$_{aryl}$), 2.35 (s, 6, Me).
213		Procedure A. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 12.27 (s, 1, OH), 8.85 (N=CH), 7.6 - 6.9 (m, 4, H$_{aryl}$); ^{13}C NMR (CDCl$_3$, 75 MHz, rt) δ 170.6, 161.5, 134.9, 133.3, 119.5, 118.7 and 117.8 (N=CH, C$_{aryl}$ excluding C$_6$F$_5$ resonances).
214		Procedure A. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 8.20 (s, 1, N=CH), 8.0 - 7.0 (m, 8, H$_{aryl}$), 3.00 (septet, 2, CHMe$_2$), 1.21 (d, 12, CHMe$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz, rt) δ 161.9 (N=CH), 149.3, 137.6, 136.1, 131.3, 128.8, 128.5, 124.1 and 123.0 (C$_{aryl}$), 28.0 (CHMe$_2$), 23.5 (CHMe$_2$).
215		Procedure A. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 8.48 (s, 1, N=CH), 7.35 - 6.95 (m, 3, H$_{aryl}$), 2.22 (s, 3, Me); ^{13}C NMR (CDCl$_3$, 300 MHz, rt) δ 153.9 (N=CH), 148.2, 130.4, 128.8, 127.6, 125.5 and 122.6 (C$_{aryl}$ excluding C$_6$F$_5$ resonances), 18.4 (Me).

| 216 | | Procedure B. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 7.99 (s, 1, CH=N), 7.7 - 6.5 (m, 6, H$_{aryl}$), 3.00 (septet, 2, CHMe$_2$), 1.19 (d, 12, CHMe$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz, rt) δ 152, 150.4, 149, 145.5, 137.8, 124.3, 123.0, 115.0 and 112.0 (N=CH and C$_{aryl}$), 27.9 (CHMe$_2$), 23.6 (CHMe$_2$). |
| 217 | | Procedure B. ^{1}H NMR (CDCl$_3$, 300 MHz, rt) δ 8.35 (s, 1, CH=N), 7.6 - 7.1 (m, 6, H$_{aryl}$), 3.08 (septet, 2, CHMe$_2$), 1.25 (d, 12, CHMe$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz, rt) δ 154.9, 148.5, 142.5, 137.8, 131.6, 130.1, 127.6, 124.2 and 122.9 (N=CH and C$_{aryl}$), 27.9 (CHMe$_2$), 23.4 (CHMe$_2$). |

<u>Example 218</u>

In a dry and oxygen free atmosphere, the allyl initiator of Example 168 (16 mg) was dissolved in dry CH$_2$Cl$_2$ (2 ml). 5-Ethylidene-2-norbornene (1.8 g) was added. The orange solution

5 warmed and darkened. After stirring for 17 hours the reaction was quenched by addition of methanol and the solid polymer filtered, washed well with methanol and dried. Yield = 1.6 g (89%). ^{1}H-NMR data confirmed that this was an addition polymer.

<u>Example 219</u>

10 <u>Synthesis of 107</u>

2,6-Dimethylthiophenol (3.0 g) was mixed with 30 ml THF. Then 0.87g NaOH was added. The mixture was stirred until all the NaOH has dissolved. THF was removed under vacuum. To the solid was added 40 ml DMF and 4.02 g of the bis toluenesulfonate ester

15 of ethylene glycol. The mixture was refluxed for 5-6 h. DMF was removed by rotary evaporator to give a white residue. Water was added to the residue and the mixture extracted with CH$_2$Cl$_2$. After removing CH$_2$Cl$_2$, a white solid remained. TLC (hexane) showed two bands. The second band from a silica-gel column was the desired

20 product.

^{1}H NMR (CDCl$_3$, δ in ppm): 2.43 (s, 12H); 2.72(s, 4H); 7.10(m, 6H).

Example 220

Synthesis of 116

9-Anthraldehyde (2.06 g) was dissolved in a minimum amount
of THF, then 1.37g anthranilic acid was added. Four drops of
5   formic acid were added as catalyst. The mixture was refluxed for
7h. TLC (5:1 hexane:ethyl acetate) gave 3 bands. The second band
is the desired product as determined by ^{1}H NMR.

Example 221

Synthesis of 117

10   10-Chloro-9-anthraldehyde (2.41 g) was dissolved in a
mixture of 30 ml THF/20 ml CDCl$_3$/50 ml toluene. To this boiling
solution was added dropwise 3.5g 2,6-diisopropylaniline 3-4 drops
of formic acid as a catalyst. The solution was refluxed for 13h.
After removing all the solvent, a dark brown thick oil was left.
15   On standing, the oil crystallized. The crystals were washed with
methanol.

^{1}H NMR (CDCl$_3$, δ in ppm): 1.40 (d, 12H); 3.35(p, 2H);
7.40(m, 3H); 7.75(m, 4H); 8.75(d, 2H); 9.05(d, 2H); 9.55(s, 1H).

Example 222

20   Synthesis of 118

10-Chloro-9-anthraldehyde was (2.41 g) was dissolved in 50
ml toluene, and to the hot solution was added 2.0 g of methyl
anthranilate (in THF) dropwise. After refluxing for 6h, a yellow
solid precipitated. The solid was isolated by filtration,
25   followed by washing with methanol. The solid was dissolved in 2-
3ml CDCl$_3$ and after column separation, golden yellow crystals were
obtained. ^{1}H NMR showed it is a pure product.

^{1}H NMR (DMF-d7, δ in ppm): 4.20(s, 3H); 6.50(d, 1H); 6.82(t,
1H); 7.20(t, 1H); 7.63(t, 2H); 7.80(t, 2H); 8.10(s, 1H); 8.30(d,
30   1H); 8.30(d, 2H); 9.20(d, 2H).

92

Example 223

In a dry and oxygen free atmosphere, the allyl initiator of
Example 168 (16mg) was dissolved in dry CH_2Cl_2 (2 ml).
Dicyclopentadiene (2 ml) was added. The orange solution darkened.
5   After stirring for 72 h the volatiles were removed from the
reaction under vacuum. After addition of methanol the solid
polymer precipitated and was filtered, washed well with methanol
and dried. Yield = 0.29 g (15%). The product was insoluble at
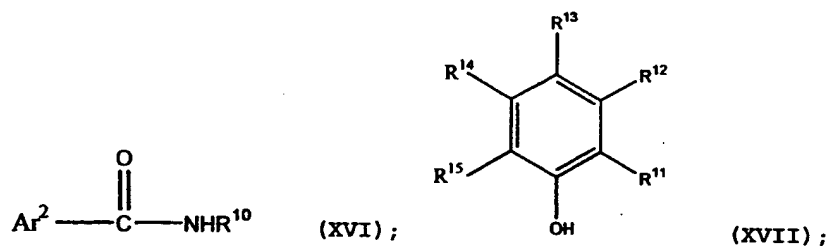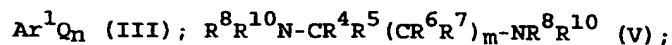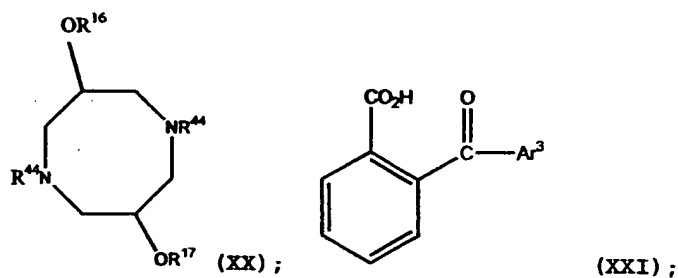room temperature in common organic solvents.

10

CLAIMS

What is claimed is:

1. A process for the polymerization of an olefin, comprising:

   (a) contacting a polymerizable monomer consisting essentially of ethylene, a norbornene or a styrene, and a catalyst system comprising the product of mixing in solution a zerovalent tricoordinate or tetracoordinate nickel compound (II) which has at least one labile ligand, and all ligands are neutral, an acid of the formula HX (IV), and a first compound selected from the group consisting of:

$$Ar^1Q_n \; (III); \quad R^8R^{10}N\text{-}CR^4R^5(CR^6R^7)_m\text{-}NR^8R^{10} \;\; (V);$$

$$Ar^2\text{---}\overset{\overset{\textstyle O}{\|}}{C}\text{---}NHR^{10} \quad (XVI);$$

(XVII);

$$H_2N\text{---}\diagup\diagdown\text{---}CO_2H \quad (XVIII);$$

(XIX);

(XX);

(XXI);

(XXII);

(XXIII);

(XXIV);

(XXV);

(XXVI); $Ar^9HN \longrightarrow S \longrightarrow NHAr^{10}$ (XXVII);

$R^{22}R^{23}R^{24}P$ (XXVIII);

(XXXVI);

and $R^8S\text{-}CR^4R^5(CR^6R^7)_m\text{-}SR^5$ (XXXVII);

and wherein:

X is a noncoordinating anion;

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;
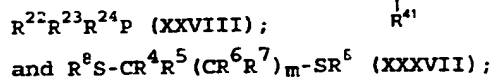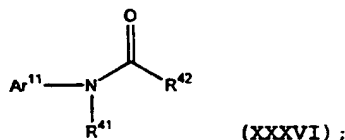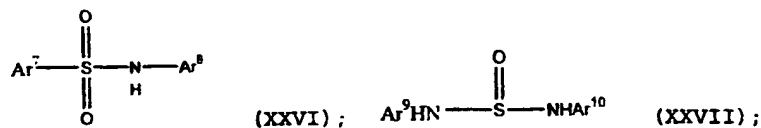
R^{43} is hydrogen or alkyl;

n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^9 is independently hydrogen or hydrocarbyl; and

each R^3 is independently a monovalent aromatic moiety;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl,
substituted hydrocarbyl or an inert functional group whose E_s is
about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl
5   containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or
hydrocarbyl;

Ar^4 is an aryl moiety;
10   Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety or
-CO_2R^{25}, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;
15   R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or -$C(O)$-NR^{41}-Ar^{11};

R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups
substituted by one or more alkoxy groups, each alkoxy group
20   containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl
moiety.

2. A catalyst for the polymerization of ethylene, a
norbornene, or a styrene, comprising, the product of mixing in
25   solution a zerovalent tricoordinate or tetracoordinate nickel
compound (II) which has at least one labile ligand and all ligands
are neutral, an acid of the formula HX (IV), and a first compound
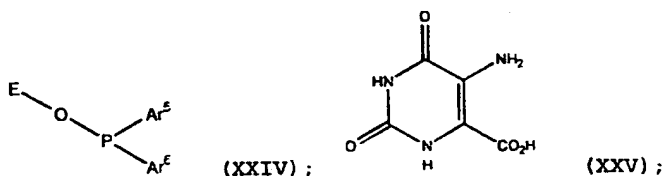selected from the group consisting of:

Ar^1Q_n (III); $R^8R^{10}N$-$CR^4R^5(CR^6R^7)_m$-NR^8R^{10} (V);

30

96

(XX) ;

(XXI) ;

(XXII) ;

5   (XXIII) ;

(XXIV) ;

(XXV) ;

(XXVI) ;

(XXVII) ;

10

$R^{22}R^{23}R^{24}P$ (XXVIII) ;

(XXXVI) ;

and $R^{8}S-CR^{4}R^{5}(CR^{6}R^{7})_{m}-SR^{8}$ (XXXVII) ;

and wherein:

     X is a noncoordinating anion;

15   Ar^{1} is an aromatic moiety with n free valencies, or diphenylmethyl;

     each Q is $-NR^{2}R^{43}$ or $-CR^{9}=NR^{3}$;

     R^{43} is hydrogen or alkyl

     n is 1 or 2;

20   E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^3 is independently a monovalent aromatic moiety;

each R^9 is independently hydrogen or hydrocarbyl; m is

5   1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

10   each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

15   R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 cr less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

20   Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

25   Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety, -CO_2R^{25}, or Ar^7 and Ar^8 taken together are a divalent aromatic moiety and wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

30   R^{41} is hydrogen or hydrocarbyl;

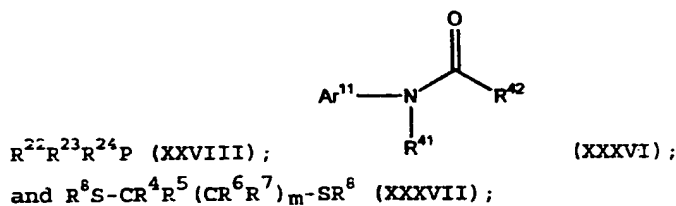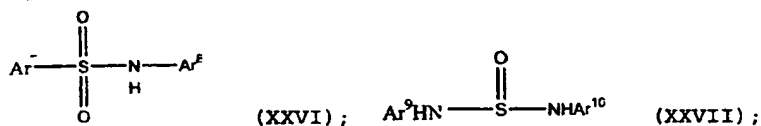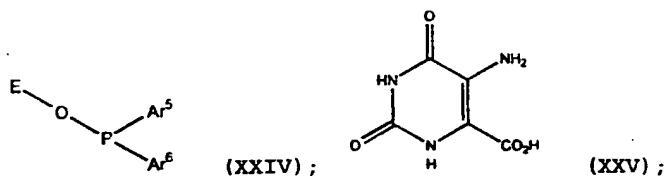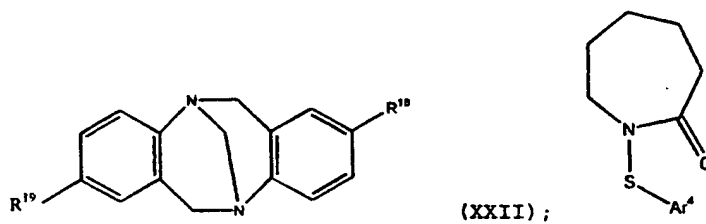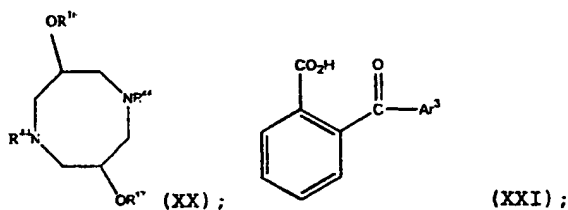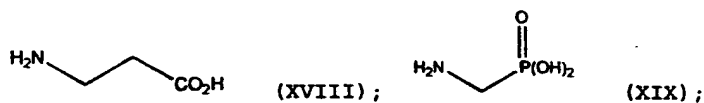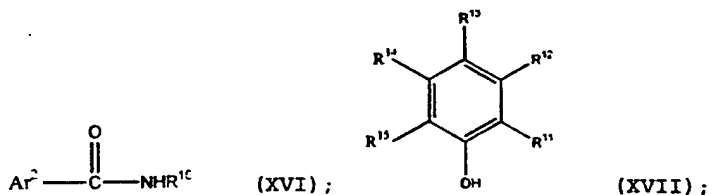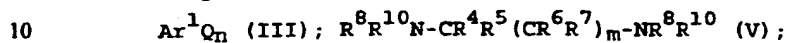R^{42} is hydrocarbyl or -C(O)-NR^{41}-Ar^{11};

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

35   R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety;

R^{44} is aryl;

and provided that the molar ratio of (III), (V) (XVI),
(XVII), (XVIII), (XIX), (XX), (XXI), (XXII), (XXIII), (XXIV),
(XXV), (XXVI), (XXVII), (XXVIII), (XXXVI) or (XXXVII):(II) is
about 0.5 to about 5, and the molar ratio of (IV):(II) is about

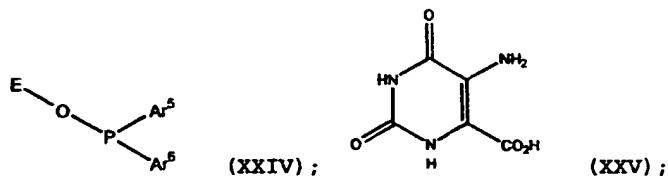5   0.5 to about 10.

3. A process for the polymerization of an olefin,
comprising, contacting ethylene, a norbornene, or a styrene with a
nickel [II] complex of a first compound selected from the group
consisting of:

10   Ar^1Q_n (III); $R^8R^{10}N-CR^4R^5(CR^6R^7)_m-NR^8R^{10}$ (V);

(XVI);

(XVII);

(XVIII);

(XIX);

15

(XX);

(XXI);

(XXII);

(XXIII);

20

(XXIV);

(XXV);

99

$$Ar^7-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\underset{H}{N}-Ar^8 \quad \text{(XXVI)};$$

$$Ar^9HN-\overset{\overset{O}{\|}}{S}-NHAr^{10} \quad \text{(XXVII)};$$

$$R^{22}R^{23}R^{24}P \quad \text{(XXVIII)};$$

$$Ar^{11}-\underset{\underset{R^{41}}{|}}{N}-\overset{\overset{O}{\|}}{C}R^{42} \quad \text{(XXXVI)};$$

and $R^8S\text{-}CR^4R^5(CR^6R^7)_m\text{-}SR^8$ (XXXVII);

and wherein:

X is a noncoordinating anion;

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

R^{43} is hydrogen or alkyl

n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^3 is independently a monovalent aromatic moiety;

each R^9 is independently hydrogen or hydrocarbyl; m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

5   Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety, - CO_2R^{25}, or Ar^7 and Ar^8 taken together are a divalent aromatic moiety and wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

10   R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or $-C(O)-NR^{41}-Ar^{11}$;

R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20

15 carbon atoms, and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety.

4. A process for the polymerization of olefins, comprising, contacting ethylene, a norbornene or a styrene with a nickel

20 containing first compound of the formula $[L^1_qL^2_rL^3_sL^4_tNi]^+X^-$ (XXXIII), wherein:

L^2 is a first monodentate neutral ligand coordinated to said nickel, L^2 is a second monodentate neutral ligand coordinated to said nickel which may be said first monodentate neutral ligand

25 and r is 0 or 1, or L^1 and L^2 taken together are a first bidentate neutral ligand coordinated to said nickel and r is 1;

L^3 and L^4 taken together are a π-allyl ligand coordinated to said nickel, L^3 and L^4 taken together are

30   (XXXII)
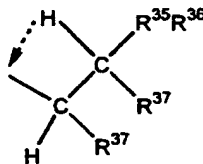
coordinated to said nickel, or L^3 is a third neutral monodentate ligand selected from the group consisting of ethylene, a norbornene and a styrene or a neutral monodentate ligand which can be displaced by an olefin, and L^4 is R^{38};

35   q, s and t are each 1;

X is a relatively non-coordinating anion;

said first monodentate neutral ligand and said first

bidentate neutral ligand are selected from the group consisting of

Ar^1Q_n (III); $R^8R^{10}N-CR^4R^5(CR^6R^7)_m-NR^8R^{10}$ (V);

(XVI) ; (XVII) ;

(XVIII) ; (XIX) ;

(XX) ; (XXI) ;

(XXII) ;

(XXIII) ;

(XXIV) ; (XXV) ;

(XXVI) ; (XXVII) ;

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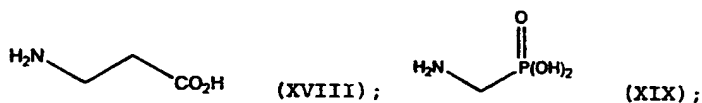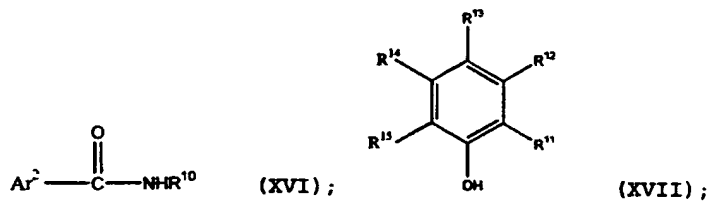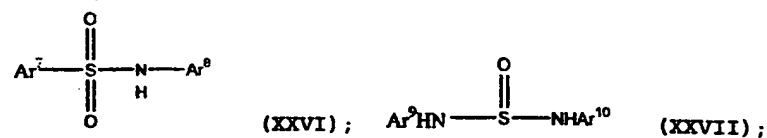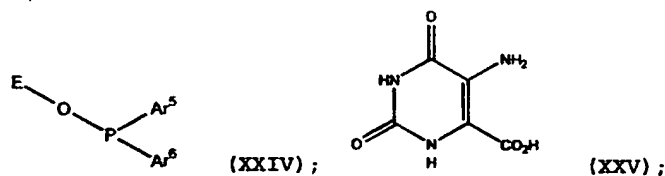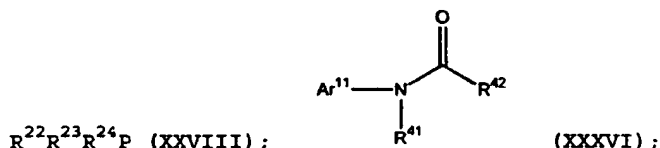
$$\text{(XXXVI):}$$

$$R^{22}R^{23}R^{24}P \text{ (XXVIII);}$$

and $R^6S-CR^4R^5(CR^6R^7)_m-SR^8$ (XXXVII);

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is $-NR^2R^{43}$ or $-CR^9=NR^3$;

R^{43} is hydrogen or alkyl

n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^9 is independently hydrogen or hydrocarbyl; and

each R^3 is independently a monovalent aromatic moiety;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E$_s$ is about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety or -CO$_2$R^{25}, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

R^{41} is hydrogen or hydrocarbyl;

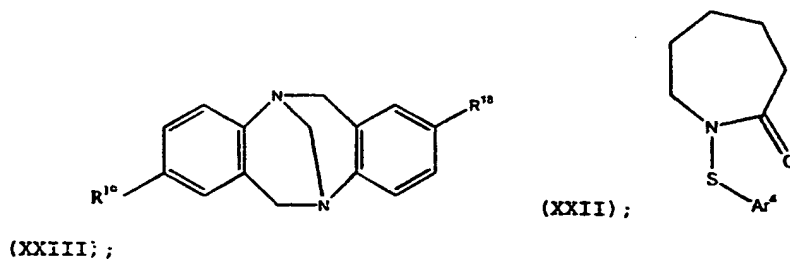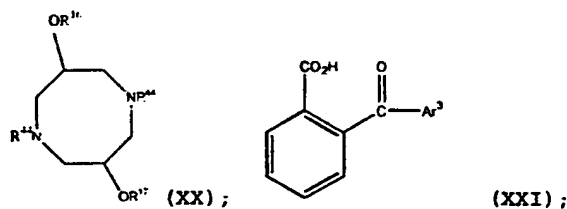R^{42} is hydrocarbyl or -C(O)-NR^{41}-Ar^{11};

R^{22} and R^{23} are each independently phenyl groups

5   substituted by one or more alkoxy groups, each alkoxy group

containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl

moiety;

R^{35} is hydrocarbylene;

10   R^{36} is hydrogen, alkyl, or -C(O)R^{39};

each R^{37} is hydrocarbyl or both of R^{37} taken together are

hydrocarbylene to form a carbocyclic ring;

R^{38} is hydride, alkyl or -C(O)R^{39};

R^{39} is hydrocarbyl; and

15   R^{44} is aryl.

5. A compound of the formula [L^1_qL^2_rL^3_sL^4_tNi]$^+$X$^-$ (XXXIII),

wherein:

L^1 is a first monodentate neutral ligand coordinated to

said nickel, L^2 is a second monodentate neutral ligand coordinated

20   to said nickel which may be said first monodentate neutral ligand

and r is 0 or 1, or L^1 and L^2 taken together are a first bidentate

neutral ligand coordinated to said nickel and r is 1;

L^3 and L^4 taken together are a π-allyl ligand coordinated

to said nickel, L^3 and L^4 taken together are

(XXXII)

coordinated to said nickel, or L^3 is a third neutral monodentate

ligand selected from the group consisting of ethylene, a

norbornene and a styrene or a neutral monodentate ligand which can

30   be displaced by an olefin, and L^4 is R^{38};

X is a relatively non-coordinating anion;

q, s and t are each 1;

said first monodentate neutral ligand and said first

bidentate neutral ligand are selected from the group consisting of

35   Ar^{1}Q$_n$ (III); R^{8}R^{10}N-CR^{4}R^5(CR^{6}R^7)$_m$-NR^{8}R^{10} (V);
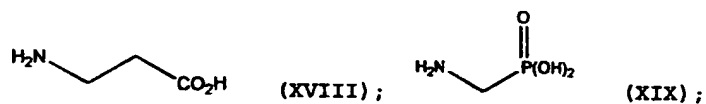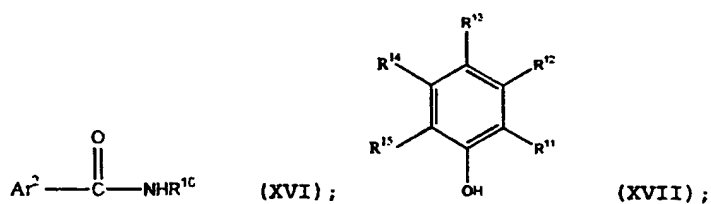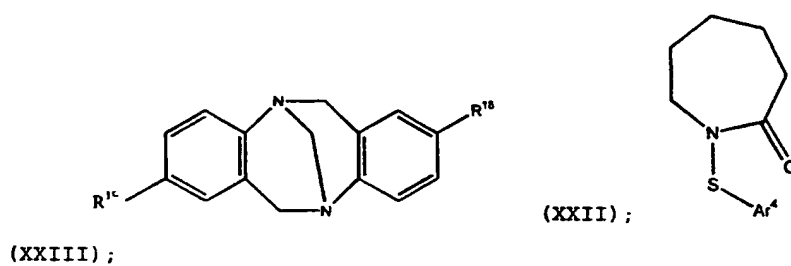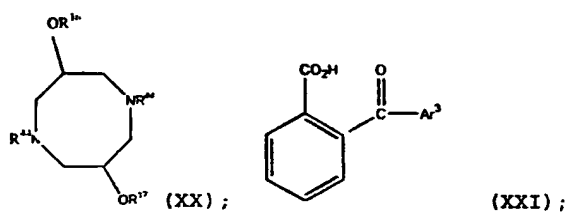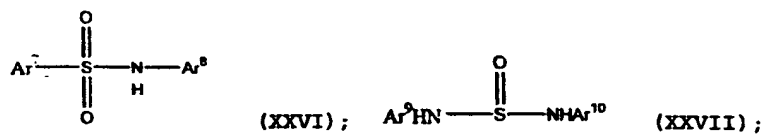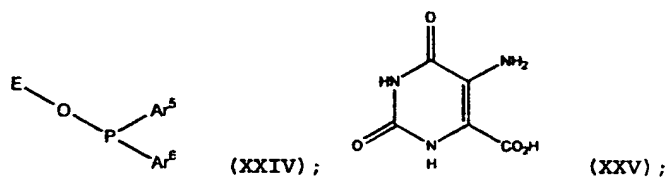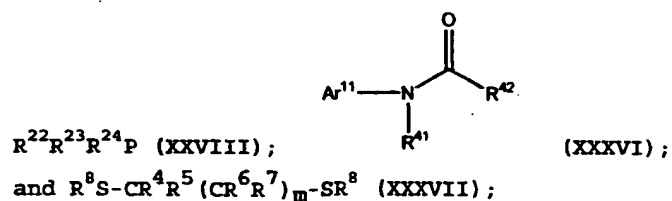
Ar^2—C—NHR^{16} (XVI);   (XVII);

H_2N ~~~ CO_2H (XVIII); H_2N—P(OH)$_2$ (XIX);

(XX);   (XXI);

(XXIII);   (XXII);

E—O—P   (XXIV);   (XXV);

(XXVI);   (XXVII);

$R^{22}R^{23}R^{24}P$ (XXVIII);   (XXXVI);

and R^8S-$CR^4R^5(CR^6R^7)_m$-SR^8 (XXXVII);

Ar^1 is an aromatic moiety with n free valencies, or diphenylmethyl;

each Q is -NR^{2}R^{43} or -CR^9=NR^3;

R^{43} is hydrogen or alkyl

5   n is 1 or 2;

E is 2-thienyl or 2-furyl;

each R^2 is independently hydrogen, benzyl, substituted benzyl, phenyl or substituted phenyl;

each R^9 is independently hydrogen or hydrocarbyl; and

10   each R^3 is independently a monovalent aromatic moiety;

m is 1, 2 or 3;

each R^4, R^5, R^6, and R^7 is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^8 is independently hydrocarbyl or substituted

15   hydrocarbyl containing 2 or more carbon atoms;

each R^{10} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{12}, R^{13}, and R^{14} are each independently hydrogen,

20   hydrocarbyl, substituted hydrocarbyl or an inert functional group;

R^{11} and R^{15} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E$_s$ is about -0.4 or less;

each R^{16} and R^{17} is independently hydrogen or acyl

25   containing 1 to 20 carbon atoms;

Ar^3 is an aryl moiety;

R^{18} and R^{19} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

30   Ar^5 and Ar^6 are each independently hydrocarby;

Ar^7 and Ar^8 are each independently an aryl moiety;

Ar^9 and Ar^{10} are each independently an aryl moiety or -CO$_2$R^{25}, wherein R^{25} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

35   R^{41} is hydrogen or hydrocarbyl;

R^{42} is hydrocarbyl or -C(O)-NR^{41}-Ar^{11};

R^{44} is aryl;

R^{22} and R^{23} are each independently phenyl groups

substituted by one or more alkoxy groups, each alkoxy group

containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl

5   moiety;

R^{35} is hydrocarbylene;

R^{36} is hydrogen, alkyl, or $-C(O)R^{39}$;

each R^{37} is hydrocarbyl or both of R^{37} taken together are

hydrocarbylene to form a carbocyclic ring;

10   R^{38} is hydride, alkyl or $-C(O)R^{39}$; and

R^{39} is hydrocarbyl.

6. The process as recited in claim 1 or 3 wherein the molar

ratio of (III):(II) is about 0.5 to 5, and the molar ratio of

(IV):(II) is about 0.5 to about 10.

15   7. The process or catalyst as recited in claim 1, 2, 3, 4 or

5 wherein X is BF_4^-, PF_6^-, BAF^-, or SbF_6^-.

8. The process or catalyst as recited in claim 1, 2 or 3

wherein (II) is bis(η^4-1,5-cyclooctadienyl)nickel[0].

9. The process as recited in claim 1, 3 or 4 wherein an

20   olefin is ethylene.

10. The process as recited in claim 1, 3 or 4 wherein an

olefin is norbornene.

11. The process as recited in claim 1, 3 or 4 wherein an

olefin is styrene.

25   12. The process as recited in claim 1, 3 or 4 wherein an

olefin is a combination of styrene and norbornene, and a copolymer

of styrene and norbornene is produced.

13. The process, compound or catalyst as recited in claim 1,

2, 3, 4 or 5 wherein said first compound or said first monodentate

30   neutral ligand is (III).

14. The process, compound or catalyst as recited in claim 13

wherein:

n is 1, Q is $-CR^9=NR^3$, R^9 is hydrogen, Ar^1 is 9-

anthracenyl, and R^3 is 2-carbamoylphenyl or 2,6-diisopropylphenyl;

35   n is 2 and Q is $-CR^9=NR^3$, R^3 is 2,6-disubstituted phenyl

in which substitutents are halo, alkyl, or halo and alkyl, Ar^1 is

p-phenylene, and R^9 is hydrogen;

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n is 1, Q is $-CR^9=NR^3$, R^9 is hydrogen, R^3 is 2,6-
dimethylphenyl, and Ar^1 is pentafluorophenyl; or

n is 1, Q is $-CR^9=NR^3$, R^9 is hydrogen, R^3 is 2,6-
diisopropylphenyl, and Ar^1 is 2-hydroxy-1-naphthyl.

15. The process, compound or catalyst as recited in claim 13
wherein:

n is 1, Q is $-NR^2R^{43}$, R^2 is $-CH=CPh_2$, R^{43} is hydrogen, and
Ar^1 is 2,6-diisopropylphenyl;

n is 1, Q is $-NR^2R^{43}$, R^2 is $-CH=CPh_2$, R^{43} is hydrogen and
Ar^1 is 2-carbamoylphenyl;

n is 2, Q is $-NR^2R^{43}$, R^2 is hydrogen, R^{43} is hydrogen,
and Ar^1 is 1,8-napthylylene;

n is 1, Q is $-NR^2R^{43}$, R^2 is $-CH=CPh_2$, R^{43} is hydrogen, and
Ar^1 is 2-methoxycarbonylphenyl;

n is 1, Q is $-NR^2R^{43}$, R^2 is hydrogen, R^{43} is hydrogen,
and Ar^1 is 2-carboxyphenyl;

n is 1, Q is $-NR^2R^{43}$, R^2 is $-CH=CPh_2$, R^{43} is hydrogen, and
Ar^1 is 1-anthraquinonyl;

n is 1, Q is NR^2R^{43}, R^2 is $-CH=CPh_2$, R^{43} is hydrogen, and
Ar^1 is
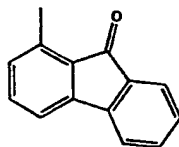
, or

wherein (III) is
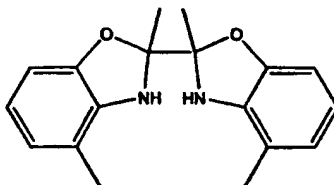
16. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (V).

17. The process or catalyst as recited in claim 16 wherein:
m is 1, all of R^8, R^4, R^5, R^6 an R^7 are hydrogen, and
both of R^{10} are 2,6-diisopropylphenyl; or

m is 1, all of R^8, R^4, R^5, R^6 an R^7 are hydrogen, and
both of R^{10} are cyclohexyl.

18. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XVI).

19. The process or catalyst as recited in claim 18 wherein:

Ar^2 is 2-(N-2,2-diphenylethenylamino)phenyl and R^{10} is hydrogen;

Ar^2 is phenyl and R^{10} is 2,6-diisopropylphenyl;

Ar^2 is 2-pyridyl and R^{10} is hydrogen; or

Ar^2 is 3-hydroxy-2-pyridyl and R^{10} is hydrogen.

20. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XVII).

21. The process, compound or catalyst as recited in claim 20 wherein:

R^{11} and R^{15} are t-butyl and R^{12}, R^{13} and R^{14} are hydrogen;

R^{11}, R^{13} and R^{15} are t-butyl and R^{12} and R^{14} are hydrogen;

R^{11} and R^{15} are phenyl and R^{12}, R^{13} and R^{14} are hydrogen; or

R^{11} is t-butyl and R^{12} and R^{14} are hydrogen, R^{13} is methoxy, and R^{15} is 2-hydroxy-3-t-butyl-5-methoxyphenyl.

22. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XVIII).

23. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XIX).

24. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XX) both of R^{44} are phenyl.

25. The process, compound or catalyst as recited in claim 24 wherein:

both of R^{16} and R^{17} are hydrogen; or

both of R^{16} and R^{17} are acetyl.

26. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XXI).

27. The process, compound or catalyst as recited in claim 26 wherein Ar^3 is 2-aminophenyl.

28. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXII).

29. The process, compound or catalyst as recited in claim 28
wherein R^{18} and R^{19} are both methyl or both hydrogen.

30. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXIII).

31. The process, compound or catalyst as recited in claim 30
wherein Ar^4 is phenyl.

32. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXIV).

33. The process, compound or catalyst as recited in claim 32
wherein both of Ar^5 and Ar^6 are phenyl or wherein both of Ar^5 and
Ar^6 are cyclohexyl.

34. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXV).

35. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXVI).

36. The process, compound or catalyst as recited in claim 35
wherein Ar^7 is p-tolyl or phenyl and Ar^8 is 2,6-diisopropylphenyl.

37. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXVII).

38. The process, compound or catalyst as recited in claim 37
wherein:

Ar^9 and Ar^{10} taken together are 1,8-naphthylylene; or
Ar^9 is $-CO_2CH_3$ and Ar^{10} is

39. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXVIII).

40. The process, compound or catalyst as recited in claim 39
wherein:

all of R^{22}, R^{23} and R^{24} are 2,4,6-trimethoxyphenyl;

both of R^{22} and R^{23} are 2,3,6-trimethoxyphenyl and R^{24} is
ethyl;

all of R^{22}, R^{23} and R^{24} are 2,6-dimethoxyphenyl; or

both of R^{22} and R^{23} are 2,3,6-trimethoxyphenyl and R^{24} is
isopropyl.

41. The process, compound or catalyst as recited in claim 39
wherein at least one of R^{22}, R^{23} and R^{24} is substituted and that a
sum of σ and $\sigma*$ constants for at least one of R^{22}, R^{23} and R^{24} is
about -0.50 or less.

42. The process, compound or catalyst as recited in claim 41
wherein R^{24} is an aryl moiety, all of R^{22}, R^{23} and R^{24} are
substituted, and said sum of said σ and $\sigma*$ constants for each of
R^{22}, R^{23} and R^{24} is about -0.50 or less.

43. A compound of the formula
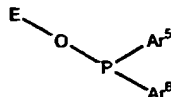
(XXIV)

wherein:

E is 2-thienyl or 2-furyl;

Ar^5 and Ar^6 are each independently hydrocarbyl.

44. The compound as recited in claim 43 wherein both of Ar^5
and Ar^6 are phenyl or wherein both of Ar^5 and Ar^6 are cyclohexyl.

45. The process as recited in claim 3 or 4 carried out in a
solvent.

46. The process as recited in claim 1, 3 or 4 carried out at
a temperature of about -20°C to about 100°C.

47. The process, compound or catalyst as recited in claim 1,
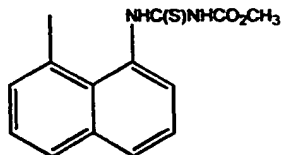2, 3, 4 or 5 wherein said first compound or said first monodentate
neutral ligand is (XXXVI).

48. The process, compound or catalyst as recited in claim 1,
2, 3, 4 or 5 wherein (XXXVI) is
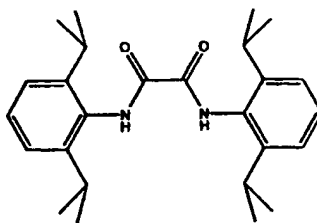
49. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein said first compound or said first monodentate neutral ligand is (XXXVII).

50. The process, compound or catalyst as recited in claim 49 wherein both of R^8 are aryl moieties and all of R^4, R^5, R^6, R^7 and R^8 are hydrogen.

51. The process as recited in claim 50 wherein both of R^8 are 2,6-dimethylphenyl.

52. The process, compound or catalyst as recited in claim 1, 2, 3, 4 or 5 wherein X is BAF.

53. The process or compound as recited in claim 4 or 5 wherein r is 1.

54. The process or compound as recited in claim 4 or 5 wherein r is 0.

55. The process or compound as recited in claim 54 wherein (XXXIII) is a dimer with bridging L^1 ligands.

56. The process, compound or catalyst as recited in claim 13 wherein:

n is 2

Q is $-CR^9=NR^3$;

Ar^1 is diphenylmethyl;R^9 is hydrogen

and R^3 is selected from the group consisting of 2,6-diisopropylphenyl, 2-carbamoylphenyl, 2-methoxycarbonylphenyl, 1-anthraquinolyl, 2,6-dimethylphenyl and 1-fluoren-9-onyl.

57. The process as recited in claim 3 wherein said nickel [II] complex is a π-allyl complex.

58. The process as recited in claim 4 wherein L^3 and L^4 taken together are a π-allyl group.

59. The compound as recited in claim 5 wherein L^3 and L^4 taken together are a π-allyl group.

60. The process as recited in claim 57 or 58 wherein a Lewis acid is also present.

61. The process as recited 1, 3 or 4 wherein at least 2 or more norbornenes are present, to form a copolymer.

62. The process as recited in claim 1, 3 or 4 wherein at least 2 or more styrenes are present to form a copolymer.

5   63. The process as recited in claim 1, 3 or 4 wherein at least one styrene and at least norbornene are present to form a copolymer.

64. The process as recited in claim 61 wherein a nobornene present is 5-ethylidene-2-norbonene.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F10/02   C08F12/04   C08F32/04   C08F4/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 117, no. 23, 14 June 1995, WASHINGTON, XP002015954 JOHNSON, L. K. ET AL.: "New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and alpha-Olefins" see page 6414 - page 6415 ---	1-9
X	MACROMOLECULAR SYMPOSIA, vol. 89, 1 January 1995, pages 393-409, XP000509182 TAUBE R ET AL: "THE CATALYSIS OF THE STEREOSPECIFIC BUTADIENE POLYMERIZATION BY ALLYL NICKEL AND ALLYL LANTHANIDE COMPLEXES A MECHANISTIC COMPARISON"	5
A		1-4, 6-42, 45-64

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| X | Further documents are listed in the continuation of box C. | X | Patent family members are listed in annex. |

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 October 1996	25. 10. 96

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4 716 205 A (KLABUNDE ULRICH) 29 December 1987 see the whole document -----	1-64

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Information on patent family members

Int   onal Application No

PCT/US 96/11131

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